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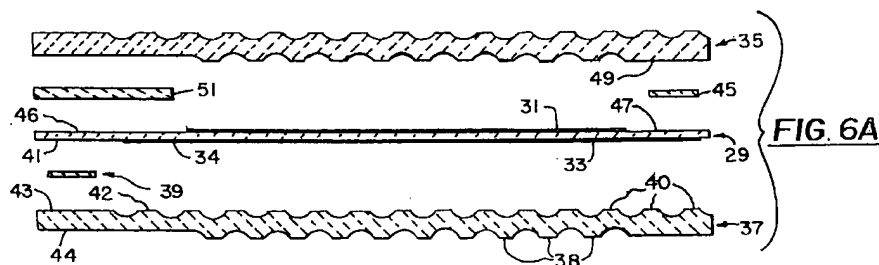
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(54) Separation of oxygen from an oxygen-containing gas

(57) An electrochemical device for separating oxygen from an oxygen-containing gas comprises a plurality of planar ion-conductive solid electrolyte plates and electrically-conductive gas-impermeable interconnects assembled in a multi-cell stack. Electrically-conductive anode and cathode material is applied to opposite sides of each electrolyte plate. A gas-tight anode seal is bonded between the anode side of each electrolyte plate and the anode side of the adjacent interconnect. A regulating electrode, applied to the anode side of each

electrolyte plate between the anode seal and the edge of the anode, eliminates anode seal failure by maintaining the 24-hour anode seal power density below about $1.5 \mu\text{W}/\text{cm}^2$. A gas-tight seal is applied between the cathode sides of each electrolyte plate and the adjacent interconnect such that the anode and cathode seals are radially offset on opposite sides of the plate. The combination of regulating electrodes and offset seals is particularly effective in eliminating anode seal failure.



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CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] Not applicable.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

10 [0002] Not applicable.

BACKGROUND OF THE INVENTION

[0003] Ion-conducting inorganic oxide ceramic materials of certain compositions transport or permeate ions at high temperatures, and this phenomenon is the basis for practical applications in fuel cells, gas analysis and monitoring, and the separation of gas mixtures. In a number of such practical applications, oxygen ions migrate as current under an imposed potential gradient through an oxygen ion-conducting electrolyte from the cathode side, where oxygen ions are generated by reduction of oxygen or other gases, to the anode or oxygen side, where the oxygen ions are consumed to form oxygen or other gases.

[0004] Oxygen ion-conducting solid electrolytes can be constructed in tubular, flat plate, and honeycomb or monolith multicell configurations. The flat plate configuration, in which a plurality of planar electrolytic cells are stacked to operate in electrical series, is favored in many applications for ease of assembly and compact dimensions. The practical application of ion conductor systems for gas separation, regardless of design configuration, requires that the cells operate under a differential pressure and/or differential gas composition between the feed side (cathode) and the permeate side (anode). In the separation of oxygen from an oxygen-containing gas, for example, the pressure and/or gas composition of the oxygen-containing feed gas and the oxygen-depleted discharge gas (also defined as nonpermeate gas) can differ from the pressure and/or gas composition of the oxygen produced at the anode (also defined as permeate gas), depending on the stack design and product requirements. Gas-tight seals between selected structural components of the system therefore are required to maintain product gas purity, whether the product is oxygen-depleted discharge gas or high purity oxygen produced at the anode.

[0005] An oxygen ion-conducting system having a disk or planar stack configuration is described in U.S. Patent 4,885,142 in which an oxygen-containing gas is introduced through axial feed pods, flows radially across stacked electrolyte disks, and is discharged through an axial discharge port preferably centrally located. Oxygen product is withdrawn through a separate series of axial discharge pods. The feed and product gases are segregated by interfitting parts of the disk assembly, which is described to form a substantially sealing relationship. The stack operates with no differential pressure across the cells and the use of sealants is not disclosed. A similar system is disclosed in papers by J. W. Sutor et al entitled "Oxygen Separation From Air Using Zirconia Solid Electrolyte Membranes" in *Proceedings of the 23rd Intersociety Energy Conversion Conference*, Vol. 2, ASME, New York, 1988, pp. 273-277, and by D. J. Clark et al entitled "Separation of Oxygen By Using Zirconia Solid Electrolyte Membranes" in *Gas Separation and Purification*, 1992, Vol.6, No. 4, p. 201-205.

[0006] U.S. Patent 5,186,806 discloses a planar solid electrolyte cell configuration in which alternating plates and gas distribution support members are stacked in series. In one configuration the plates are made of ion-conducting non-porous material and the support members are made of non-porous electrically-conducting material. A series of ports and bosses in the support members coincide with ports in the electrolyte plates to yield a flow configuration in which feed air flows radially across the cathode sides of the electrolyte plates in an inward direction, and the oxygen-depleted air is withdrawn axially through a centrally-located conduit formed by congruent ports in the electrolyte plates and support members. Oxygen formed on the anode sides of the electrolyte plates flows radially outward and is withdrawn through a plurality of axial conduits formed by separate congruent ports in the electrolyte plates and distribution members. Sealing between the oxygen side and feed gas sides of the stack components according to the disclosure is accomplished by direct contact between electrolyte plates and flat bosses on the support members, and also at the stack periphery by contact between continuous flat raised rings on the support members and the flat electrolyte plates. No sealant is described in the seal regions formed by direct contact between regions of the support members and the electrolyte plates. The seal regions formed by the bosses in contact with the anode side and the cathode side of each electrolyte plate are radially and circumferentially offset, but the corresponding peripheral seals are congruent or directly opposed.

[0007] An ion conducting device having a plurality of electrolyte plates in a stacked configuration is disclosed in U.S. Patent 5,298,138 in which supporting electrically-conducting interconnects are not used. The electrolyte plates are separated by alternating spacers made of electrolyte material which is attached near the edges of the plates by glass sealant to allow crossflow feed. While this stack design is simplified by eliminating interconnects, the electrolyte plates are

not supported in the central region, which allows operation only at very small pressure differentials between the anode and cathode sides of the cells.

[0008] European Patent Application Publication No. 0 682 379 A1 discloses a series planar electrochemical device for gas separation in which alternating electrolyte plates and electrically-conducting interconnects are assembled in a stack configuration. The anode and cathode in electrical contact with opposite sides of each electrolyte plate are radially coextensive, i.e. congruent. The interconnects contain channels designed such that feed gas flows through the cathode side in crossflow mode and oxygen formed on the anode side is withdrawn in a crossflow mode in a flow direction perpendicular to the feed gas flow. The interconnects and electrolyte plates are connected by glass sealing areas parallel to the channels in the interconnects. Portions of the anode and cathode seals are directly opposed on each electrolyte plate.

[0009] A technical report entitled "Stacking Oxygen Separation Cells" by C. J. Morrissey in *NASA Tech Brief*, Vol. 15, No. 6, Item #25, June 1991 describes planar stacked electrolyte cells comprising alternating electrolyte plates and gas distribution interconnects. The anode and cathode on each electrolyte plate are directly opposed across the electrolyte plate, i.e., they are congruent. Glass seals are used between each electrolyte plate and the adjacent interconnects, and the seals are directly opposed across the electrolyte plate, i.e., they are congruent. This design includes a nonporous electrically insulating layer located at the edge of the stack between the interconnects.

[0010] Planar stacked electrolyte cells comprising alternating electrolyte plates and interconnects having embossed gas passageways are disclosed in a technical report entitled "Thinner, More Efficient Oxygen Separation Cells" by C. J. Morrissey in *NASA Tech Brief*, Vol. 17, No. 4, Item #100, April 1993. Air is introduced into the cells through axial manifolds passing through the stack which provide feed in radial flow across the cathode sides of the cells. Oxygen-depleted air is withdrawn through a centrally-located axial manifold. Oxygen product from the anode sides of the cells is withdrawn through additional axial manifolds passing through the stack at locations circumferentially disposed between the air feed manifolds. The anode and cathode on each electrolyte plate appear to be directly opposed across the electrolyte plate, i.e., they are congruent. While seals are not specifically discussed in the text, it appears from the drawings that seals between each electrolyte plate and the adjacent interconnects would be directly opposed across the electrolyte plate, i.e., they are congruent.

[0011] Thus the state of the art in the design of stacked ion-conducting electrolytic cells teaches methods for sealing the anode and cathode sides of the cells to prevent cross-contamination of feed and product gases. Sealing has proved difficult, however, at the high temperatures and electrochemically active conditions encountered in these systems. The practical application of ion conductor systems for gas separation, regardless of design configuration, requires that the cells operate under differential pressures and/or differential gas compositions between the feed and product sides of the cells, and this in turn requires robust gas-tight seals between the stack components. This need is addressed in the invention which is described in the specification below and defined by the claims which follow.

BRIEF SUMMARY OF THE INVENTION

[0012] The invention pertains to an electrochemical device for the recovery of oxygen from an oxygen-containing gas, and in particular to an improved operating method for planar series electrolytic cells.

[0013] The invention is a method for separating oxygen from an oxygen-containing gas which comprises contacting the oxygen-containing gas with a first surface of a planar solid electrolyte capable of transporting oxygen ions, supplying electrons to the first surface of the solid electrolyte by a cathode in electrical contact with a portion of the first surface, and electrochemically reducing oxygen in the oxygen-containing gas by consuming electrons to produce oxygen ions. The resulting oxygen ions are transported as current through the solid electrolyte by imposing an electrical potential across the planar solid electrolyte, and oxygen gas is produced at a second surface of the solid electrolyte by consuming oxygen ions and producing electrons. The electrons are conducted from the second surface by an anode in electrical contact with a portion of the second surface, and the electrons are conducted from the anode by a gas impermeable electrically conducting interconnect which is in electrical contact with the anode. Oxygen gas is collected in a cavity bounded at least in part by the second surface of the solid electrolyte, the gas impermeable electrically conducting interconnect, and a gas-tight anode seal disposed between a portion of the second surface of the solid electrolyte and an opposing portion of the electrically conducting interconnect. Oxygen gas is withdrawn from the cavity and an oxygen-depleted gas is withdrawn from contact with the first surface of the planar solid electrolyte. The 24-hour anode seal power density is maintained below about $1.5 \mu\text{W}/\text{cm}^2$, preferably by one or more regulating electrodes. At least one of the regulating electrodes may be an extended portion of the anode or alternatively may be an electrode which is separate from the anode. Both types of regulating electrodes may be employed concurrently. Preferably at least one of the regulating electrodes is disposed between the anode and the anode seal. Optionally at least one of the regulating electrodes is not disposed between the anode and the anode seal.

[0014] The pressure of the oxygen gas generated at the second surface of the solid electrolyte may be different than the pressure of the oxygen-containing gas at the first surface of the solid electrolyte. In one embodiment, the oxygen-

containing gas comprises air, and the oxygen gas is withdrawn as a high purity pressurized product at a pressure at least 5 kPa greater than the pressure of the oxygen-containing gas. Alternatively the oxygen-containing gas contains less than 20.9 vol% oxygen. In another embodiment, the oxygen-containing gas comprises argon and an argon product depleted in oxygen is withdrawn after contacting the oxygen-containing gas with the first surface of the solid electrolyte and after the oxygen is removed by reduction (ionization) and transport across the solid electrolyte. The argon product may be obtained at a pressure equal to or greater than the pressure of the oxygen gas in the cavity formed by the anode sides of the electrolyte plate and interconnect.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0015]

Fig. 1 is a plan view of the cathode side of an electrolyte plate of the present invention.

Fig. 2 is a plan view of the anode side of an electrolyte plate.

Fig. 3 is a plan view of the anode side of an alternative electrolyte plate.

Fig. 4 is a plan view of the cathode side of an interconnect.

Fig. 5 is a plan view of the anode side of an interconnect.

Figs. 6A and 6B are exploded section views which include single electrolytic cells.

Figs. 7A and 7B are assembled section views of multiple series electrolytic cells.

Fig. 8 is a quarter section through the insulating support, electrode, and cathode seal of an assembled stack.

Fig. 9 is a complete section through the insulating support, electrode, and cathode seal of an assembled stack.

Fig. 10 is a schematic isometric view of a complete electrolyte stack.

Fig. 11 is a plot of flow efficiency vs. operating time for Examples 2 and 3 in the Specification.

Fig. 12 is a plot of flow efficiency vs. stack differential pressure for Examples 3 and 4 in the Specification.

Fig. 13 is a schematic drawing of a three layer test cell as a representative portion of an anode seal for determining the anode seal current.

Fig. 14 is a plot of the 24-hour anode seal power density vs test period duration for Example 5.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Separation devices based on oxygen ion-conducting solid electrolytes have practical applications in the production of high-purity oxygen from air and in the removal of residual oxygen from inert gases such as argon or nitrogen. In either application, the solid electrolyte is operated with a difference in gas pressure and/or gas composition between the feed (cathode) side and the product or permeate (anode) side of the electrolyte. The strength of the components in such a separation device and the stability of the required gas-tight seals between these components must be sufficient to sustain practical pressure and/or composition differentials over the economic lifetime of the device.

[0017] Separation devices based on oxygen ion-conducting solid electrolytes can be constructed in tubular, flat plate, and honeycomb or monolith configurations. The flat plate configuration, in which a plurality of planar electrolyte cells are stacked to operate in electrical series, is favored in many applications for ease of assembly, cost effectiveness, and compact dimensions. The flat plate configuration must be designed with the appropriate component strength and seal integrity to operate at a pressure differential and/or gas composition differential between feed and product gas streams while maintaining purity requirements of the product gas stream. The present invention utilizes a flat plate stack design and method of operation which meets these requirements.

[0018] Difficulties have been experienced in the past in maintaining such seals as reported in the cited references of the prior art summarized above. Anode seal failure readily occurs in stack designs in which the seals on the anode and cathode sides of the electrolyte plate are directly opposed. This failure was observed as delamination at the interface between the seal material and the anode side of the electrolyte plate. It is believed that this seal failure may be the result of stray or residual anodic current passing through the seal.

[0019] In the present invention, several improvements in the stack design were identified which reduce or eliminate anode seal failure. One of these improvements is the use of one or more regulating electrodes in contact with each electrolyte plate which modify the electrolyte potential in the seal region such that current flow through the anode seal is minimized. A regulating electrode can be an extension of the anode beyond the edge of the projected area of the cathode on the opposite side of the electrolyte plate. Alternatively, a separate regulating electrode or grounding strip can be placed on the electrolyte plate between the anode and the anode seal. An extended anode and a separate grounding strip can be used in combination if desired. The term regulating electrode as used herein is defined as any electrode material which is in electrical contact with the electrolyte plate, is located on an area of the electrolyte plate such that the area has no cathode material on the opposite side of thereof, and maintains the 24-hour anode seal power density below about $1.5 \mu\text{W}/\text{cm}^2$. This 24-hour anode seal power density is maintained preferably by establishing electrical con-

tact between the regulating electrode and the anode side interconnect. The projection of an area on the anode side of the plate covered by a regulating electrode onto the cathode side of the electrolyte plate will not contact or overlap cathode material. Typically the regulating electrode or electrodes are placed on the anode side of the electrolyte plate. If desired, a regulating electrode can be located on the cathode side of the electrolyte plate if such a regulating electrode (a) is not in electrical contact with the cathode, (b) is not in electrical contact with the cathode side interconnect, and (c) is in electrical contact with the anode side interconnect. At least a portion of such a cathode-side regulating electrode preferably is directly opposite the anode seal.

[0020] Another improvement is the radial offset of the anode and cathode seals such that the seals do not overlap on opposite sides of each electrolyte plate. This feature, defined herein as offset seals, requires a specific cell design geometry as described below. It has been found that a combination of offset seals and regulating electrodes is particularly effective in reducing or eliminating anode seal failure by controlling the 24-hour anode seal power density below about $1.5 \mu\text{W}/\text{cm}^2$.

[0021] The planar or flat plate design of the present invention utilizes alternating electrolyte plates and electrically-conductive interconnects which define individual electrochemical cells which operate in electrical series and isolate the feed and product gases as described above. The key component of each electrochemical cell is the electrolyte plate and associated electrodes which distribute the electrical potential and flow of electrons over the surface of the plate. The electrolyte plates should be as thin as possible while maintaining sufficient strength to operate at the required pressure differentials.

[0022] The electrolyte plates are planar and are stacked in the axial direction; the shape of the plates in the radial direction can be circular, square, rectangular, or any other planar geometrical shape. The preferred electrolyte plate of the present invention is generally square with rounded corners as shown in plan view in Fig. 1, which is the feed or cathode side of the plate. Electrode material 1, which is cathode material forming the cathode, is applied to the central region of the electrolyte plate such that continuous unelectroded regions 3 and 5 remain. Unelectroded region 5 surrounds opening 7 which extends through the plate. The term unelectroded region means any region of the electrolyte plate which has no electrode material applied thereon. The electrolyte material is a multicomponent ionic conducting metallic oxide comprising an oxide of at least two different metals or a mixture of at least two different metal oxides wherein the multicomponent metallic oxide demonstrates ionic conductivity at device operating temperatures, typically greater than about 500°C . Any solid oxygen ion-conducting electrolyte known in the art can be used; representative electrolytes include yttria stabilized zirconia, strontia-doped ceria, gadolinia-doped ceria, and bismuth vanadium oxide. The cathode material is formed from an oxidation-resistant metal, an alloy, or a multicomponent mixed conducting oxide. Particularly useful electrode material includes lanthanum strontium cobaltite (LSCO), $\text{La}_x\text{Sr}_{1-x}\text{CoO}_{3-z}$, wherein x ranges from 0.2 to 1 and z is a number which renders the compound charge neutral. The LSCO can be used with an intermediate coating of lanthanum strontium cobaltite and silver or silver-palladium alloy which is applied to the electrode surface. The coating can be applied as a paste and sintered, or can be applied by screen printing or equivalent methods, by sputtering, or by other techniques well known in the art. The thickness of the cathode is about 0.1 to 100 microns. Representative dimensions of the electrolyte plate are 5 to 20 cm in width or diameter and 0.01 to 0.065 cm in thickness.

[0023] The anode side of the electrolyte plate is shown in plan view in Fig. 2. Electrode material 9 is applied around opening 7 and is surrounded by continuous unelectroded region 11 having a width of d_2 . Width d_2 is less than width d_1 of the cathode side of Fig. 1, and the additional width or extension of electrode 9 on the anode side is a regulating electrode as earlier defined. Typically the difference between d_1 and d_2 is about 0.1 to 2.0 cm and defines an extended anode which serves as the regulating electrode. A further definition of the extended anode is a portion of electrode material which is contiguous with and in electrical contact with the anode, and is not congruent and not coextensive with the cathode on the opposite side of the electrolyte plate.

[0024] An alternative anode side of the electrolyte plate is given in plan view in Fig. 3. Electrode material 13 is applied to the electrolyte plate and has the same shape and at least the same peripheral dimensions as electrode material 1 of Fig. 1. Separate regulating electrode 15 is applied between electrode 13 and the outer portion of unelectroded region 11. Regulating electrode 15 is also known as a grounding strip, which is defined as a regulating electrode not in direct contact with the anode. Optionally, electrode 13 is slightly larger than electrode 1 of Fig. 1. Opening 7 corresponds to opening 7 of Fig. 1. Width d_3 is similar to width d_2 of Fig. 2, and width d_3 is less than width d_1 of the cathode side of Fig. 1. The anode preferably uses electrically conducting material similar to that of the cathode described above and the regulating electrode described below, although different electrically conducting material can be used for any of these three electrode types.

[0025] The distribution of gas across the cathode side of the electrolyte plate, the withdrawal of oxygen from the anode side of the plate, and the transport of electrons from the anode side of one electrolyte plate to the cathode side of an adjacent electrolyte plate are promoted by planar interconnects having generally similar outside dimensions as the electrolyte plate. The interconnects are made of an oxidation resistant, gas-impermeable material having a thermal expansion coefficient comparable to that of the electrolyte, a high electronic conductivity, and low ionic conductivity. The

material can be a multicomponent, electronically conducting multicomponent metallic oxide, a metal or metal alloy, or a mixture of the two. Suitable electronically conducting oxides include lanthanum strontium chromite, lanthanum calcium manganite and lanthanum calcium chromite. Lanthanum strontium manganite (LSM), $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, is a preferred material for the interconnects.

[0026] The cathode side of an interconnect is shown in plan view in Fig. 4, wherein the interconnect has a continuous generally flat peripheral region 17 and an opening 19 to the opposite side of the interconnect. The interconnect generally has the same shape and size as the electrolyte plates of Figs. 1-3. A continuous generally flat region 21 surrounds opening 19. Opening 19 typically is the same or similar diameter as opening 7 in the electrolyte plates of Figs. 1-3. A plurality of raised areas 23, characterized in this embodiment as frustoconical bosses or as spherical segments with flattened tops, which also may be described as pins, are disposed between flat regions 17 and 21. The continuous depressed or non-raised areas between the raised areas in conjunction with an adjacent electrolyte plate form a cavity in flow communication with flat peripheral region 17 as described below. Alternatives to raised areas 23 can be used, such as ribs, raised rectangular or triangular areas, and the like, which perform essentially the same function as raised areas 23. The tops of raised areas 23 and flat region 21 are generally coplanar, and this plane is above the plane formed by flat region 17.

[0027] The opposite or anode side of the interconnect is shown in plan view in Fig. 5. A continuous generally flat region 25 is disposed around the periphery of the interconnect, and a plurality of raised areas 27, characterized in this embodiment as frustoconical bosses or spherical segments with flattened tops, which also may be described as pins, are disposed between generally flat region 25 and opening 19. The continuous depressed or non-raised areas between the raised areas in conjunction with an adjacent electrolyte plate form a cavity or interconnected cavities in flow communication with opening 19 as described further below. Alternatives to raised areas 27 can be used, such as ribs, channels, and the like, which perform essentially the same function as raised areas 27. Continuous grounding rib 28 surrounds the raised areas and electrically contacts the regulating electrode as described below. The tops of raised areas 27, the top of grounding rib 28, and flat region 25 are generally coplanar.

[0028] A single electrolytic cell is formed by an electrolyte plate having an anode and a cathode, and the adjacent surfaces of two interconnects joined by the appropriate gas-tight anode and cathode seals and electrical connections. An exploded sectional view of a single electrolytic cell is given in Fig. 6A and is not necessarily to scale. Partial electrolyte plate 29, which corresponds to section I-I of Figs. 1 and 2, has cathode portion 31 and anode portion 33 applied to the cathode and anode sides respectively. Anode portion 33 extends further in an outward radial direction than cathode portion 31, and this extended portion forms regulating electrode portion 34. Regulating electrode portion 34 is a part of the complete regulating electrode formed by the extension of anode 9 of Fig. 2 beyond cathode 1 of Fig. 1 in a radial outward direction. This extension is defined such that width d_2 of Fig. 2 is less than width d_1 of Fig. 1. Grounding rib 42 makes electrical contact with regulating electrode 34 when the stack is assembled. Preferably the ratio L/t is greater than about 10, where L is the width of regulating electrode portion 34 of Fig. 6A, i.e. the difference between d_1 and width d_2 , and t is the thickness of electrolyte plate 29. The ratio L/t is selected such that the 24-hour anode seal power density (defined below) across anode seal 39 is less than about $1.5 \mu\text{W}/\text{cm}^2$.

[0029] The anode seal power density is defined as the product of the anode seal potential measured in Volts and the anode seal current density measured in Amperes/cm. The anode seal potential is measured during operation of the stack as described below. The anode seal current density is measured in a separate test cell arrangement as further described below wherein the test cell is operated at the stack seal potential and the stack operating temperature. The value of the anode seal power density measured at about 24 hours of the anode seal current density test operation (described below) is defined herein as the 24-hour anode seal power density.

[0030] The anode seal potential is defined as the electrical potential difference measured between an electrical contact on the interconnect which is adjacent to the anode side of the electrolyte and a reference electrode located on the electrolyte in the vicinity of the anode seal. Further specifications defining the anode seal potential include the following. The reference electrode is located on the cathode side surface of the electrolyte plate directly opposite from the anode seal, where the area of electrical contact does not extend beyond the region defined by a projection of the anode seal onto the cathode side of the electrolyte plate. The electrical contact to the interconnect which is in direct contact with the anode seal is made on the cathode side surface directly opposite from the anode seal. This area of electrical contact does not extend beyond the region defined by a projection of the anode seal onto the cathode side of the interconnect. With reference to Fig. 6A, for example, the anode seal potential would be measured between location 46 on electrolyte plate 29 and location 44 on interconnect 37. The reference electrode is of the same type (composition, morphology, and method of making) as the anode. In addition, the oxygen absolute partial pressure of the gas in contact with the reference electrode differs from the oxygen absolute partial pressure of the gas in contact with the anode by no more than 5% of the oxygen absolute partial pressure of the gas in contact with the anode. The anode seal potential is measured under steady state non-transient conditions at the normal cell operating temperature, typically between 600°C and 850°C , and with the normal operating current density flowing through the electrolyte from anode to cathode, typically $50\text{--}1500 \text{ mA}/\text{cm}^2$.

[0031] The placement of the interconnect contact and reference electrode is such that the absolute value of the zero-current seal potential is minimized, and the minimized value preferably is less than about 0.1 mV. The zero-current seal potential is defined as the potential measured between the interconnect contact and the reference electrode under the same conditions as the measurement of the seal potential, but with zero steady-state current flowing through the cell.

Such a zero-current potential is generated, for example, by temperature gradients in the electrolyte, and thus the zero-current potential is minimized by placing the reference electrode as close as possible to the interconnect contact. If the absolute value of the zero-current seal potential is not reduced to less than about 0.1 mV by judicious placement of the reference electrode, the seal potential is corrected by subtracting the zero-current seal potential from the seal potential, and redefining the seal potential as this difference.

[0032] The current density through the anode seal caused by the anode seal potential defined above is small compared to the total current density through a stack containing multiple electrolytic plates, and is therefore more difficult to measure directly. In order to measure the anode seal current density, a representative portion of the seal must be extracted and isolated, and the current density through the seal measured under the same seal potential as the anode seal potential measured in the stack at the same temperature.

[0033] For this purpose, a representative portion of the seal can be defined as a test cell comprising a fragment of the interconnect material bonded with the seal material to an electroded fragment of an electrolyte plate as described later with respect to Example 5 and Fig. 13. The test cell should have a uniform cross-section along all axes perpendicular to the seal interface, and should provide a geometrically well-defined and quantified seal area of at least 0.5 cm². In order for the electrochemical characteristics of the seal to be as representative as possible, the preparation of the test cell should as closely duplicate the materials and process history of a stack as possible.

[0034] To ensure this duplication, the interconnect fragment should have the same thickness, composition, and fabrication history as the interconnect, and is preferably a piece of an interconnect itself from the anode seal region (land). The electrolyte fragment should have the same thickness, composition, and processing history as an electrolyte plate, and should be covered on one side only with a test electrode having the same composition and fabrication history as a cathode in a stack. The anode seal surface of the interconnect fragment and the unelectroded side of the electrolyte fragment should be bonded with the same sealant as found in a stack, and should have the same composition, thickness, and fabrication history as a stack.

[0035] There are several conceivable ways to prepare such a test cell. One method would be to fabricate a stack with an additional portion of the cathode applied to the cathode side of the electrolyte plate opposite the anode-side seal with an area of at least 0.5 cm². Following fabrication, this stack would be cut apart using a ceramic abrasion saw to remove a portion of the seal region meeting the dimensional criteria described above. Another method would be to prepare a test cell from separate fragments of the stack components. An interconnect fragment having uniform cross section and meeting the dimensional criteria of the test cell, would be cut from the seal region of an interconnect. An electrolyte plate fragment, of the same lateral dimensions as the interconnect fragment, would be fabricated in exactly the same way as other electrolyte plates, and prepared with a cathode test electrode (on one side only) in exactly the same way as other electrochemical cells. These fragments would then be bonded using the sealant under exactly the same conditions as fabrication of a stack.

[0036] A third method would be to prepare a test cell from separate components as above, but to use a specially prepared pellet of the interconnect material, prepared in exactly the same manner as an interconnect. In this case the electrolyte, electrode, and seal would be sized accordingly, and prepared as above.

[0037] In all these test cell methods, it is very important to ensure that the seal area is well defined, and that there are no alternate current paths. For example, drips of sealant around the edge of the test cell which connects the electrode directly to the interconnect must be eliminated. One way to prevent current bypass is to grind away any excess sealant following the preparation of the test cell. Another way is to make the electrolyte fragment of the test cell slightly larger in lateral dimension than the interconnect fragment, while leaving the electrode the same size as the interconnect fragment. In all these test cell methods, the test electrode cross-sectional area, the anode seal cross-sectional area, and the interconnect cross sectional area should be approximately equal. The term approximately equal as used here means that the cross-sectional areas of any two components differ by no more than 20%. For example, the test electrode cross-sectional area and the anode seal cross-sectional area should differ by no more than 20%.

[0038] The anode seal current density is defined as the anode seal current determined above divided by the anode seal cross-sectional area in the test cell. The anode seal power density is calculated as the product of the anode seal potential measured in Volts and the anode seal current density measured in Amperes/cm².

[0039] The anode seal current density test cell as shown in Fig. 13 should be tested at the same temperature as the operation of the stack by applying an essentially constant potential across the test cell such that the test cell anode seal potential is equivalent to the anode seal potential previously measured in the stack. Current density is determined as a function of the time of operation of the test cell, and the value after about 24 hours of continuous test cell operation is used to calculate the 24-hour anode seal power density.

[0040] Interconnect portions 35 and 37 of Fig. 6A correspond to section III-III of Figs. 4 and 5. Anode seal 39 is dis-

posed between continuous unelectroded region 41 (corresponding to continuous unelectroded region 11 of Fig. 2) and continuous generally flat region 43 (corresponding to continuous generally flat region 25 of Fig. 5). Cathode seal 45 is disposed between continuous unelectroded region 47 (corresponding to continuous unelectroded region 5 of Fig. 1) and continuous generally flat region 49 (corresponding to continuous generally flat region 21 of Fig. 4). A preferred material for seals 39 and 45 is a glass-ceramic derived from a lithium aluminosilicate (LAS) glass, which is a material known in the art for use in seals as described for example in an article by T. J. Headly and R. E. Loehman entitled "Crystallization of a Glass-Ceramic by Epitaxial Growth" in *Journal of the American Ceramic Society*, Vol. 67, pp. 620-625, 1984.

[0041] Anode seal 39 and cathode seal 45 form gas-tight seals between the respective areas of the electrolyte plate and the interconnect when the stack is assembled as described below. The gas tight seals maintain product gas purity and prevent product loss, and prevent or minimize the mixing of feed and product streams. The seals prevent or minimize gas mixing due to pressure differential and/or gas composition differential among the feed, permeate, and nonpermeate streams. The gas-tight seals also serve to bond the electrolyte plates and interconnects together in the stack as shown below. The seals can be cofired and bonded directly to the electrolyte plates and interconnects, or alternatively one or more additional cofired materials can be used.

[0042] Optionally an electrically insulating support is disposed between the cathode side of electrolyte plate 29 and the cathode side of interconnect 35, and a portion of this support is denoted as support 51. This support eliminates damaging stresses on electrolyte plate 29 when the gas pressure on the anode side of the electrolytic cell is greater than the gas pressure on the cathode side of the cell. Support 51 may or may not be gas tight, and is not applied continuously as explained in more detail below.

[0043] An exploded sectional view of an alternative single electrolytic cell is given in Fig. 6B. Components of this alternative electrolytic cell are identical to those of Fig. 6A except for the electrode material applied to the anode side of electrolyte plate 52. Anode portion 53 has a smaller extension in the outward radial direction than anode portion 33 of Fig. 6A, and separate regulating electrode portion 55 is applied to the anode side of electrolyte plate 52. Regulating electrode portion 55 is a part of regulating electrode 15 of Fig. 3. Grounding rib 56 makes electrical contact with regulating electrode portion 55 when the stack is assembled. This grounding rib typically is continuous and makes continuous contact with the regulating electrode, but optionally may be discontinuous, i.e. formed as a series of raised areas arranged in a circular pattern which are in electrical contact with the regulating electrode.

[0044] A plurality of the elements described in Fig. 6A are assembled by arranging alternating electrolyte plates and interconnects into a stack, and the stack is fired to yield a plurality of electrolytic cells in series, three of which are shown in Fig. 7A. In the process of assembling each cell, an electrically conducting material is applied to the surfaces of the raised areas on each interconnect as defined by elements 23 of Fig. 4 and 27 of Fig. 5. When the stack is fired, this conducting material bonds to the raised areas on the interconnects and to the electrodes on each electrolyte plate. The conducting material is shown in Fig. 7 as conformal layers 57 disposed between interconnect portion 59 and the cathode on electrolyte plate 61, and conformal layers 63 disposed between adjacent interconnect portion 65 and the anode on electrolyte plate 61. The conformal layers provide electrical connections between the electrodes and the adjacent interconnects, and also provide mechanical support for the electrolyte plate. The conducting material is preferably silver initially applied as an ink before firing.

[0045] In the alternative embodiment described above, a plurality of the elements described in Fig. 6B are assembled into a stack and fired to yield a plurality of electrolytic cells in series, three of which are shown in Fig. 7B. The cells of Fig. 7B are identical to those of Fig. 7A except for different regulating electrodes. In Fig. 7A, regulating electrodes 67 are radial extensions of the anodes on the respective electrolyte plates wherein each anode extends radially beyond the edge of the cathode on the opposite side of the electrolyte plate. This was described earlier with respect to Figs. 1 and 2 wherein the regulating electrode is the anode extension having a width equal to the difference between width d_1 and width d_2 . In Fig. 7B, individual regulating electrode portions 69 are disposed between each electrolyte plate and the adjacent interconnects. The complete regulating electrode for this alternative is shown as element 15 in Fig. 3, wherein width d_3 is less than width d_1 in Fig. 1.

[0046] A preferred feature of this embodiment of the present invention is the use of regulating electrodes which reduce or eliminate anode seal failure by maintaining the 24-hour anode seal power density at less than about $1.5 \mu\text{W}/\text{cm}^2$. Anode seal failure can occur by debonding or delamination at the interface between the anode seal material and the interconnect, or alternatively by debonding or delamination at the interface between the anode seal material and the electrolyte plate.

[0047] A second feature is that each anode seal is completely offset on the electrolyte plate relative to the corresponding cathode seal. The term offset seals is defined as the geometrical seal arrangement in which the projection of any anode seal area onto the cathode side of the electrolyte plate does not contact or overlap any cathode seal. This is illustrated in Fig. 6A wherein anode seal portion 39 is disposed adjacent to the outer periphery of the electrolyte plate whereas cathode seal portion 45 is disposed adjacent to the central opening in the plate. The combination of regulating electrodes and offset seals as utilized in the present invention is particularly effective in eliminating anode seal failure.

[0048] Operation of the planar electrolytic cells as described above may require that the pressure of the oxygen product is higher than the pressure of the oxygen-containing feed gas, such that the cells operate in an oxygen pumping mode. This operation may place a significant mechanical stress on the outer region of the electrolyte plate. As earlier described, this problem is alleviated by the use of electrically insulating support 51 disposed between the cathode side of electrolyte plate 29 and interconnect 35 (Fig. 6A). This electrically insulating support reduces potentially damaging stresses on electrolyte plate 29 when the gas pressure on the anode side of the electrolytic cell is greater than the gas pressure on the cathode side of the cell. Multiple supports are shown in Fig. 7A as supports 71 and Fig. 7B as supports 73.

[0049] The electrically insulating support material should have a coefficient of thermal expansion which is substantially equivalent to the coefficient of thermal expansion of the adjacent electrolyte material or that of the adjacent interconnect material. Substantially equivalent means that the coefficients of thermal expansion of the insulating support and an adjacent material over the temperature range of about 20°C to about 750°C differ by less than about 2 micrometer / (meter · °C), preferably by less than about 1 micrometer/(meter · °C), and most preferably by less than about 0.5 micrometer/ (meter · °C). Insulating support material having lower values of Young's modulus can tolerate larger differences in the coefficient of thermal expansion compared with the electrolyte and interconnect materials, while insulating support materials with higher Young's modulus values can tolerate smaller differences in the coefficient of thermal expansion. The insulating support is prepared using one or more electrically insulating ceramics as described below. An electrically insulating ceramic is defined herein as any electrically nonconductive ceramic which does not permit the passage of electrical current when placed in an electric field (see *Modern Ceramic Engineering*, D. W. Richerson, 2nd Edition, Marcel Dekker, Inc, New York, p. 228). Mixtures of such ceramics are selected to have high electrical resistivity and to have coefficients of thermal expansion similar to those of the electrolyte and interconnect materials. Representative ceramics for use in the insulating support include but are not limited to the oxides of Mg, Al, Si, Yb, Ca, Be, Sr, Nd, Sm, Er, Eu, Sc, La, Gd, Dy, and Tm.

[0050] The insulating support can be fabricated by several different methods. In the first of these methods, the insulating support is made by preparing a mixture of inorganic oxide glass or glass-ceramic combined with one or more electrically insulating ceramics in an organic vehicle or carrier to form an ink, applying the ink to an interconnect or the electrolyte plate, and firing at above about 500°C. The firing temperature preferably approaches or reaches the melting temperature of the glass, which typically is in the temperature range of about 800° to about 1000°C. The preferred coefficient of thermal expansion of the support material after firing is between about 9 and about 15 micrometer / (meter · °C).

[0051] A typical ink composition is 70 wt% solids and 30 wt% liquid organic vehicle or carrier, although other compositions can be used as required. A preferred composition range of the solids portion of the mixture before firing (excluding the organic vehicle or carrier) contains about 0.3 to about 27 wt % of a lithium aluminosilicate glass with the remainder being the insulating ceramics magnesia (MgO) and alumina (Al₂O₃). The weight ratio of magnesia to alumina in the mixture before firing is selected to be between about 0.2 and about 8 in order to yield the preferred coefficient of thermal expansion of the insulating support material. In addition, the amount of glass is selected such that the final assembled insulating support after firing is electrically insulating.

[0052] In another method, a mixture of electrically insulating ceramics is formed into a desired shape and sintered to form an electrically insulating support. This sintered electrically insulating support is bonded to the electrolyte and interconnect by placing inorganic oxide glass or glass-ceramic between the insulating support and the electrolyte, placing inorganic oxide glass or glass-ceramic between the insulating support and the interconnect, and firing at a temperature sufficient to bond the insulating support to both the electrolyte and the interconnect. Preferably the inorganic oxide glass or glass-ceramic is a lithium aluminosilicate glass. Alternatively, the sintered electrically insulating support can be bonded to the electrolyte by cofiring at temperatures sufficient to bond the insulating support directly to the electrolyte without the use of inorganic nonmetallic glass.

[0053] The insulating support is further described in Fig. 8, which corresponds to section IV-IV of Figs. 7A and 7B. The insulating support is applied discontinuously such that one portion 75 forms a continuous support and additional portions 77 form individual supports separated by open spaces 79. This is illustrated more clearly in Fig. 9, which is an expansion of section IV-IV to a corresponding full section of the entire stack at the same axial location. Insulating support portions 81 and 83 are continuous on opposite sides of the stack, while support portions 85 and 87 are discontinuous on opposite sides of the stack. Openings 89 and 91 allow cross flow of feed gas through the stack, as described more fully later, such that oxygen-containing feed gas flows through openings 89 while oxygen-depleted gas exits the stack through openings 91. The section of Fig. 9 also shows cathode 93 and cathode seal 95 which surrounds central opening 97.

[0054] The overall assembly and operation of the electrolytic cell stack is illustrated by the schematic isometric view of Fig. 10, which is not to scale. The cell stack is formed by a series of alternating electrolyte plates 95 with appropriate anodes and cathodes (not shown), interconnects 97 and insulating support material 99, with negative end plate 101 and positive end plate 103. Positive and negative electrical connections provide direct current to the stack, which oper-

ates at about 50 to 700 mV per cell.

[0055] Oxygen-containing feed gas flows into one side of the stack as shown, flows through the cathode sides of the cells in a crossflow mode, and the oxygen-depleted gas exits the opposite side of the stack. The insulating supports on the opposite sides of the stack direct gas in a crossflow mode as earlier described. A section through the stack shows the radial flow of oxygen product gas across the anode side of an interconnect towards the central opening 109. The central openings through the electrolyte plates and interconnects, in conjunction with the cathode seals earlier described, form a central conduit in gas flow communication with the anode side of each cell. The central conduit connects with oxygen withdrawal conduit 111 which in turn is connected with a gas-tight seal (not shown) to bottom or positive end plate 103. Alternatively, an oxygen withdrawal conduit could be connected at negative end plate 101 (not shown). If desired, oxygen product can be withdrawn from both ends of the stack (not shown).

[0056] The stack can be operated in at least two alternative modes. In the first mode, the feed gas is air and a high purity oxygen product comprising at least 99.5 vol% oxygen is withdrawn through conduit 111. The feed air typically is introduced at a pressure slightly above atmospheric which is sufficient to sustain proper air flow through the stack. Typically the oxygen is produced continuously at a pressure of at least 5 kPa above the feed pressure, which is possible by application of the offset seals, regulating electrodes, and insulating supports earlier described. The stack is operated at a temperature above 500°C.

[0057] In a second operating mode, the feed gas is an inert gas such as nitrogen or argon which contains a low concentration of oxygen as an impurity. The electrolyte cell stack is operated to remove a major portion of the oxygen such that the oxygen depleted gas flowing from the cathode sides of the cells contains typically less than about 100 ppbv to less than about 10 vol% oxygen. The flow of oxygen from conduit 111, which will be of high purity but low volume, may be a useful product as well. In this embodiment, it may be desirable to operate the stack such that the feed gas and oxygen-depleted product pressures are above the oxygen product pressure. In such a case, the use of the insulating support material in the stack would be optional because the electrolyte plates would receive sufficient mechanical support from the conformal layers and anode seals earlier described.

[0058] At higher operating pressures, the stack assembly may require end constraints to maintain stack integrity. These end constraints operate on end plates 101 and 103 to provide axial compressive forces which compensate for the tendency of the stack to separate under such pressures.

[0059] While the present invention preferably is utilized for the separation of air to recover high purity oxygen and the purification of inert gas to remove residual oxygen, the invention can be applied to any oxygen-containing gas mixture for any desired purpose or end product.

[0060] The electrolyte cell stack of the present invention can be fabricated by methods known in the art of ion conducting ceramics, for example as described in European Patent Application Publication No. 0 682 379 A1 earlier cited. The invention can be practiced with any materials known in the art and generally used in ion conductor stacks for electrolyte plates, electrodes, interconnects, and seals.

[0061] Other stack geometries can be envisioned which would be embodiments of the present invention in which regulating electrodes and offset seals are utilized to control the 24-hour anode seal power density at less than about 1.5 $\mu\text{W}/\text{cm}^2$. Regulating electrodes and offset seals can be applied with alternative stack configurations for introducing feed gas into the stack, for withdrawing oxygen-depleted gas from the cathode sides of the cells, and/or withdrawing oxygen from the anode sides of the cells.

[0062] In an alternative embodiment of the invention, electrically insulating material is incorporated into the cathode seal, and regulating electrodes are utilized as described above. The insulating material preferably is prepared by sintering a mixture of magnesium oxide (MgO) and aluminum oxide (Al_2O_3), and the insulating material is sealed to the cathode sides of the electrolyte plate and the interconnect with a glass-ceramic sealant, for example such as that derived from a lithium aluminosilicate (LAS) glass. In preparing the insulating material, aluminum oxide is used to lower the coefficient of thermal expansion of the magnesium oxide such that the coefficient of thermal expansion of the insulating material matches that of the electrolyte and interconnect materials. Some magnesium oxide spinel (MgAl_2O_4) may form in situ during sintering of the material. Alternatively, aluminum oxide and magnesium oxide can be fired at temperatures sufficiently high to form a $\text{MgO}/\text{MgAl}_2\text{O}_4$ ceramic. Alternatively, the insulating material can be cofired with the electrolyte at about 1550°C without the use of the glass sealant.

[0063] In this alternative embodiment which utilizes insulating material in the cathode seal, complete offset of the anode and cathode seals is not required, which allows additional flexibility in stack design. This embodiment can be applied to any stack design having directly opposed or partially opposed anode and cathode seals as long as the stack geometry allows the inclusion of a regulating electrode. For example, the embodiment could be applied to the planar stack design described in European Patent Application Publication No. 0 682 379 A1 cited above. The combination of an insulating cathode seal and a regulating electrode will allow control of the 24-hour anode seal power density at less than about 1.5 $\mu\text{W}/\text{cm}^2$.

EXAMPLE 1

[0064] The insulating support between the cathode sides of the electrolyte plate and the interconnect as described above can be formed by applying prior to stack assembly and firing an ink which contains precursor materials in a liquid vehicle or carrier. An ink for the formation of insulating support material upon firing was prepared as follows. 59.3g of alumina (Alcoa, SG 16), 255.7g of magnesia (Martin-Marietta, MC10-325), and 35.0g of a lithium aluminosilicate glass (Specialty Glass, SP1484-A) were combined and mixed in a stainless steel bowl. 72.0g of α -Terpineol (Kodak) and 78.0g of V-006 (Heraeus, Cermalloy Division) were mixed in a second stainless steel bowl. One third of the solid mixture was slowly added to the liquids and mixed together with a rubber spatula until all the powder was wetted. This step was repeated with the remaining powder until all the powder was incorporated. The mixture was then processed four times through a three-roll-mill to produce the final ink, using the mill spacing recorded below:

	Entry Roll Spacing	Exit Roll Spacing
First Pass	0.032 cm	0.019 cm
Second Pass	0.019 cm	0.006 cm
Third Pass	0.006 cm	<0.005 cm
Fourth (Final) Pass	0.006 cm	<0.005 cm

EXAMPLE 2

[0065] A two-cell stack was constructed and operated to demonstrate the use of a stack design incorporating offset seals and regulating electrodes. A 2-cell 7.6 cm diameter round stack was constructed from two 10 mole % strontia-doped ceria (SCO) electrolyte plates and three $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSM) interconnect plates arranged in alternating layers. The electrolyte plates were 0.025 cm thick. Both the interconnects and electrolyte plates had a central hole, and the holes aligned in the stack to form a central axial conduit which collected oxygen generated electrochemically at each anode. Each interconnect had a circumferential sealing surface 0.38 cm wide near the outer periphery of the anode side for a glass-ceramic seal. The cathode side interconnect sealing surface was located around the central hole and was also 0.38 cm wide. The electrolyte plates had non-electroded sealing surfaces on the cathode and anode sides which aligned with the corresponding interconnect sealing surfaces. The electrolyte and interconnect stack components were bonded together at these sealing surfaces with a lithium aluminosilicate (LAS) glass-ceramic to form gas-tight seals.

[0066] Anode-side and cathode-side electrodes of lanthanum strontium cobaltite (LSCO), $\text{La}_x\text{Sr}_{1-x}\text{CoO}_{3-z}$, wherein x ranges from 0.2 to 1.0 and z is a number which renders the compound charge neutral, were applied to the electrolyte plates. An overcoating of LSCO and silver-palladium alloy was applied to the electrodes. The electrodes were applied so that the anode was oversized relative to the cathode by 0.14 cm at the outer edge, such that the portion of the anode extending beyond the outer circumference of the cathode formed a regulating electrode as earlier described. In addition, a separate outer regulating electrode or grounding strip of the same electrode composition was applied outside the extended anode. The grounding strip regulating electrode was 0.18 cm wide, and was separated from the anode by a 0.13 cm wide gap of bare SCO electrolyte. The cathode area was 21 cm² per plate. Thus the anode and regulating electrode configuration was similar to those described in Figs. 3, 6B, and 7B. The insulating support of Fig. 6B was not used.

[0067] The electrodes were connected to 0.05 cm high (0.13 cm wide) ribs on the interconnect, separated by channels 0.13 cm wide. Silver was applied as a conductive layer between the top surface of the interconnect ribs and the electrode. The top surface of the ribs formed a common plane with the sealing surface for the glass-ceramic seal on both sides of the interconnect. The channels allowed oxygen to flow radially to the central collection port on the anode, and air to flow across the cathode in a crossflow mode.

[0068] One of the terminal interconnect plates or end plates was attached to a section of 0.48 cm O.D. 446 stainless steel tubing for oxygen withdrawal. The central hole in the other terminal interconnect plate or end plate was closed with a 2 inch square LSM plate attached with LAS. Air was supplied to the cathode-side of the stack at approximately 2 standard liters per minute. A voltage of approximately 1V was applied between the two terminal LSM interconnect plates at 750°C, and the stack electrical current and resulting flow rate of electrochemically generated oxygen were measured. A digital mass flow meter attached to the SS446 tubing was used to measure the flow. The anode-side pressure was controlled by a hand valve attached to the SS446 tubing and monitored by a Bourdon-tube pressure gauge.

Seal integrity was determined by calculating the flow efficiency as follows:

$$\begin{aligned} \text{flow efficiency (\%)} &= \frac{100 \times \text{measured O}_2 \text{ flow rate (std cc/min)}}{\text{theoretical O}_2 \text{ flow rate (100\% efficient)}} \\ &= \frac{100 \times \text{measured O}_2 \text{ flow rate (std cc/min)}}{\text{measured current (amps)} \times 3.75 \times N} \end{aligned}$$

where N is the number of cells in the stack and 3.75 is a conversion factor having units of (std cc/min)/(amps). The flow in std cc/min is defined at 21°C. The theoretical flow rate is realized when all current is fully utilized to produce collected oxygen product, i.e., when one molecule of oxygen is produced for every four electrons flowing through each cell, and all oxygen is collected in the absence of seal leaks.

[0069] The stack was held at a permanent differential pressure of 2 kPa (anode side pressure higher) for the first 1025 hours of operation, and subsequently at a differential pressure of 10 kPa (anode side pressure higher). Stack operation was monitored continuously for 5000 hours and the measured oxygen flow was essentially 100% of theoretical during the entire period. This indicates seal integrity and absence of detectable leaks.

EXAMPLE 3

[0070] A 2-cell 7.6 cm diameter round stack was constructed according to the procedure described in Example 2, except that the electrodes were coextensive at their outer edges on the electrolyte plates, i.e., the outer diameter of both electrodes was equivalent and there was no regulating electrode on the anode side. The cathode area was 31 cm² per plate. The stack was operated at 750°C in a manner similar to Example 2, except that a voltage of 1V was applied to the stack at a permanent differential pressure of 6.9 kPa (anode side pressure higher). Flow efficiency was monitored online for 480 hours in the same manner as described in Example 2. After operating the stack for 480 hours, the flow efficiency was measured over the differential pressure range 0 to 6.9 kPa (anode side pressure higher). Stack operation was terminated after 505 hours due to a significant loss in flow efficiency. The loss in flow efficiency was found to be the result of debonding of the interface between the LAS seal and the electrolyte on the anode-side of the electrolyte plate. The performance of the stack as a function of online operating time is shown in Fig. 11 for comparison with the performance of the stack of Example 2. This comparison demonstrates that regulating electrodes are required in stacks which utilize offset seals to provide a robust gas-tight anode seal.

EXAMPLE 4

[0071] A 5-cell 7.6 cm diameter round stack was constructed according to the procedure described in Example #2, except that five electrolyte plates and six interconnects were used. The anode was oversized relative to the cathode by 0.11 cm at the outer edge. The anode side outer grounding strip electrode was 0.19 cm wide, and was separated from the anode by a 0.10 cm wide gap of bare SCO electrolyte. The cathode area was 24 cm² per plate. An insulating support was used similar to that described with reference to Figs. 6B, 7B, 8, and 9 using material prepared according to Example 1. The insulating support material was bonded to the non-electroded periphery of the cathode side of the electrolyte and the flat area adjacent to periphery of the interconnect. Gaps were periodically left in the insulating support layer to allow air flow across the cathodes and oxygen-depleted air withdrawal from the cathodes similar to the flow configuration shown in Fig. 10. The stack was operated at 750°C in a manner similar to Example 2, except at a voltage of 2V and a permanent differential pressure of approximately 35 kPa (anode side pressure higher). After operating the stack for 1680 hours, the flow efficiency was measured over the differential pressure range 0 to 83 kPa (anode-side pressure higher) and was essentially 100% as shown in Fig. 12. This indicates excellent seal integrity which was maintained by the use of regulating electrodes, and complete integrity of the electrolyte plate which was maintained by the use of the insulating support layer. Fig. 12 also shows the operating data over a differential pressure range of 0-6.9 kPa for the stack of Example 3, which had no regulating electrodes. It is seen that flow efficiency for this stack design decreased rapidly as the differential pressure was increased.

EXAMPLE 5

[0072] To determine the maximum anode seal power density which avoided delamination or failure of the anode seal, several test cells were prepared and operated at various voltages using similar procedures for the stacks described in Examples 2, 3, and 4. Each test cell comprised a 2.5 cm diameter lanthanum strontium manganite (LSM) pellet (representative of a stack interconnect) bonded with LAS directly to a 2.6 cm diameter strontium-doped ceria (SCO) electrolyte disc, 0.038 cm thick. The electrolyte had a 4 cm² lanthanum strontium cobaltite (LSCO) electrode with an

overcoating of LSCO, silver, and silver-palladium alloy applied to the air side. The LSCO electrode and the overcoating constituted the test electrode. A porous silver layer was applied over the test electrode to act as a current collector.

[0073] For each test cell, a voltage was applied across the LSM pellet and current collector at 750°C, such that the test electrode was negatively charged, thereby simulating the configuration of the LAS and SCO in the anode-seal of a stack. The voltage and current were routinely measured, including after the initial 24 hour period of operation. The 24-hour anode seal power density is defined as the power density determined after about 24 hours of operation. The test electrode cross-sectional area was used to calculate the anode seal power density. The test electrode cross-sectional area approximated the anode seal cross-sectional area within 20%.

[0074] A schematic drawing of the test cell is shown in Fig. 13 (not to scale). Test cell assembly 201 comprised a pellet or layer 203 of LSM interconnect material bonded to electrolyte layer 205 by LAS anode seal 206. Test electrode 207 was applied to the cathode side of electrolyte layer 205 as described above. Porous silver current collector 209 was applied to the other side of LSCO test electrode 207. Test cell assembly 201 was mounted in a temperature-controlled test furnace (not shown) with the required electrical connections and appropriate gas lines for contacting air with the cathode side of the test cell. Voltage was applied across the test cell by potentiostat 211 and the actual voltage measured by potentiometer 213. The cell current was measured by ammeter 215.

[0075] At the end of a continuous operating period, each test cell was removed from test and the anode seal tested for delamination with a razor blade. Delamination of the LAS to SCO electrolyte bond indicated the failure of an anode seal in an operating stack. The data from these tests is summarized in Table 1 for essentially constant values of the applied potential across the test cell. The term essentially constant means that the absolute difference between the initial voltage and the 24 hr voltage varied by no more than 18% of the initial voltage. The relationship between the total operating time, anode seal power density after the initial operating period of about 24 hours, and anode seal integrity is plotted in Figure 14. This Example clearly demonstrates the need to operate anode-side seals at a 24-hour power density of less than about $1.5 \mu\text{W}/\text{cm}^2$ in order to maintain anode seal bond integrity and avoid delamination and seal failure.

Table 1
Summary of Test Results for Example 5

Pellet Test No.	Measured initial seal potential [mV]	Measured seal potential @ 24 hr [mV]	Measured final seal potential [mV]	Change in measured seal potential between initial and 24hr values [%]	Change in measured seal potential between initial and final values [%]	Anode seal current density @ 24hr [mA/cm ²]	24-hour anode seal power density [μW/cm ²]	total test time [hr]	Anode seal failure?
B24	584	687	708	18	21	2.75	1889.25	816	yes
B26	687	697	709	1	3	0.133	92.70	557	yes
B29	730	737	739	1	1	2.05	1510.85	552	yes
B32	44.9	39.6	53.4	12	19	0.1425	5.64	552	yes
B33	40.1	40.9	48.9	2	22	0.1125	4.60	552	yes
B39	8	8.7	8.38	9	5	0.0143	0.12	2520	NO
B40	7.5	8.4	8.30	12	11	0.0175	0.15	2520	NO
B41	7.9	8.6	8.26	9	5	0.0178	0.15	2520	NO
B42	44	47.6	53.2	8	21	0.085	4.05	240	yes
B43	44	47.5	46.3	8	5	0.0925	4.39	240	yes
B44	45	47.7	47.6	6	6	0.11	5.25	240	NO
B64	23.3	25.2	15.8	8	32	0.06	1.51	3312	NO
B65	22.1	25.0	15.8	13	29	0.065	1.62	3312	NO
B66	24.0	25.6	16.0	7	33	0.0525	1.34	3312	NO

[0076] Thus the present invention comprises several improvements in the design of planar electrolytic cell stacks which eliminate anode seal failure. One of these improvements is the radial offset of the anode and cathode seals such that the seals do not overlap on opposite sides of the electrolyte plate. This requires a specific cell design geometry as described above. Another improvement is the use of a regulating electrode on the anode side of the electrolyte plate which modifies or regulates the electrolyte potential in the seal region such that current flow through the anode seal is

minimized. This regulating electrode can be an extension of the anode beyond the outer edge of the cathode on the opposite side of the electrolyte plate. Alternatively or additionally, a separate regulating electrode can be placed on the electrolyte plate preferably between the anode and the anode seal. It has been found that a combination of offset seals and regulating electrodes is particularly effective in reducing or eliminating anode seal failure by controlling the 24-hour anode seal power density at less than about $1.5 \mu\text{W}/\text{cm}^2$. Another feature of the invention is the insulating support placed between the cathode sides of the electrolyte and interconnect which eliminates potentially damaging stresses on electrolyte plate 29 when the gas pressure on the anode side of the electrolytic cell is greater than the gas pressure on the cathode side of the cell.

[0077] The improvements of the present invention are not limited to the stack geometries disclosed herein. Regulating electrodes and offset seals can be applied to alternative stack configurations having different methods for introducing feed gas into the stack, for withdrawing oxygen-depleted gas from the cathode sides of the cells, and/or withdrawing oxygen from the anode sides of the cells. In any application, regulating electrodes and offset seals can be utilized to control the 24-hour anode seal power density at less than about $1.5 \mu\text{W}/\text{cm}^2$.

[0078] The essential characteristics of the present invention are described completely in the foregoing disclosure. One skilled in the art can understand the invention and make various modifications without departing from the basic spirit of the invention, and without deviating from the scope and equivalents of the claims which follow.

Claims

1. A method for separating oxygen from an oxygen-containing gas which comprises:

- (a) contacting the oxygen-containing gas with a first surface of a planar solid electrolyte capable of transporting oxygen ions;
- (b) supplying electrons to the first surface of the planar solid electrolyte by a cathode in electrical contact with a portion of the first surface;
- (c) electrochemically reducing oxygen in the oxygen-containing gas by consuming electrons to produce oxygen ions;
- (d) transporting the resulting oxygen ions as current through the solid electrolyte by imposing an electrical potential across the solid electrolyte;
- (e) producing oxygen gas at a second surface of the solid electrolyte by consuming oxygen ions and producing electrons;
- (f) conducting the electrons of step (e) from the second surface by an anode in electrical contact with a portion of the second surface;
- (g) conducting the electrons of step (f) from the anode by a gas impermeable electrically conducting interconnect which is in electrical contact with the anode;
- (h) collecting the oxygen gas in a cavity bounded at least in part by the second surface of the solid electrolyte, the gas impermeable electrically conducting interconnect, and a gas-tight anode seal disposed between a portion of the second surface of the solid electrolyte and an opposing portion of the electrically conducting interconnect;
- (i) withdrawing oxygen gas from the cavity;
- (j) withdrawing an oxygen-depleted gas from contact with the first surface of the planar solid electrolyte; and
- (k) maintaining the 24-hour anode seal power density below about $1.5 \mu\text{W}/\text{cm}^2$.

2. The method of Claim 1 wherein the anode seal power density is maintained at less than about $1.5 \mu\text{W}/\text{cm}^2$ by one or more regulating electrodes.

3. The method of Claim 2 wherein at least one of the regulating electrodes is an extended portion of the anode.

4. The method of Claim 2 wherein at least one of the regulating electrodes is separate from the anode.

5. The method of Claim 3 wherein at least one of the regulating electrodes is separate from the anode.

6. The method of Claim 2 wherein at least one of the regulating electrodes is disposed between the anode and the anode seal.

7. The method of Claim 1 wherein the pressure of the oxygen gas generated at the second surface of the solid electrolyte is greater than the pressure of the oxygen-containing gas at the first surface of the solid electrolyte.

8. The method of Claim 1 wherein the oxygen-containing gas is air.
9. The method of Claim 7 wherein the oxygen gas is withdrawn as a high purity pressurized product at a pressure at least 5 kPa greater than the pressure of the oxygen-containing gas.
- 5 10. The method of Claim 1 wherein the oxygen-containing gas is a gas containing less than 20.9 vol% oxygen.
11. The method of Claim 10 wherein the oxygen-containing gas comprises argon and an argon product depleted in oxygen is withdrawn after contacting the oxygen-containing gas with the first surface of the solid electrolyte and after the oxygen is removed by reduction and transport across the solid electrolyte in steps (c) and (d).
- 10 12. The method of Claim 11 wherein the argon product is obtained at a pressure equal to or greater than the pressure of the oxygen gas in the cavity of step (h).

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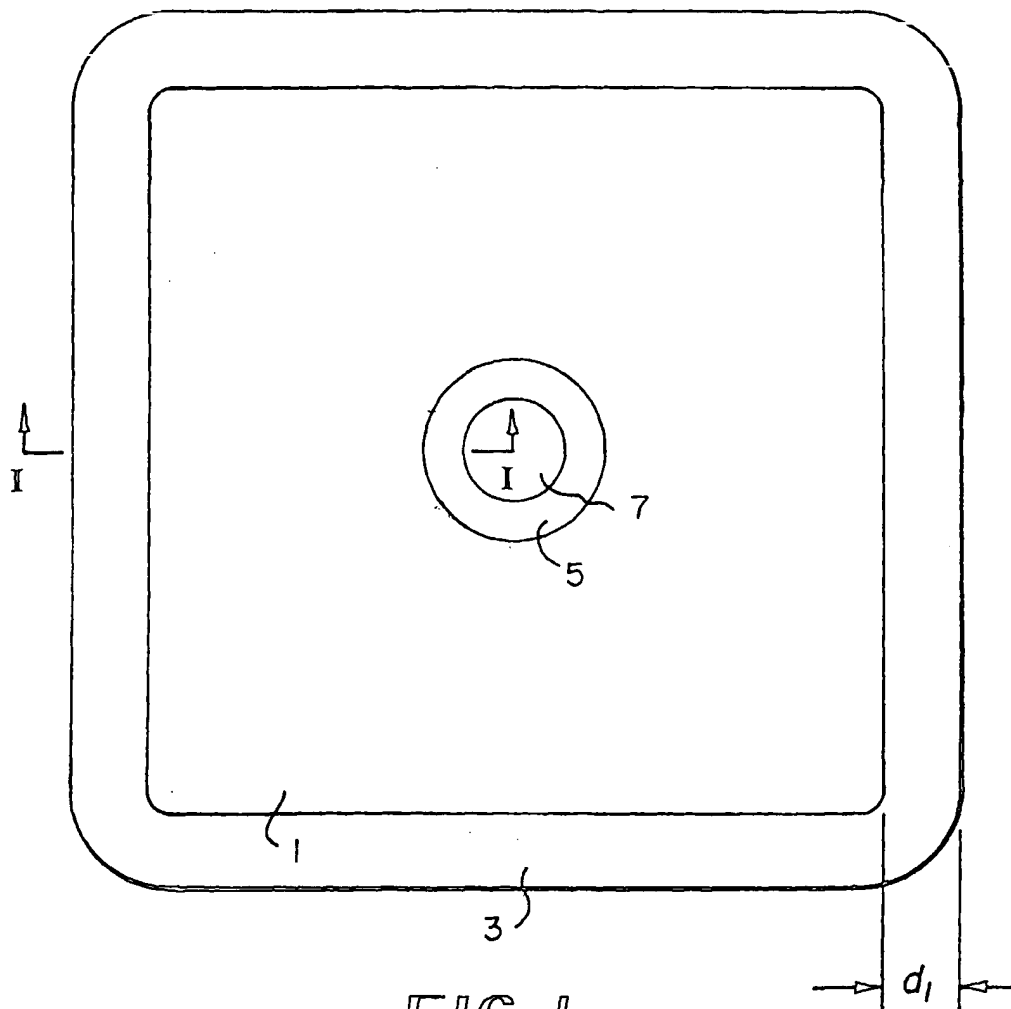
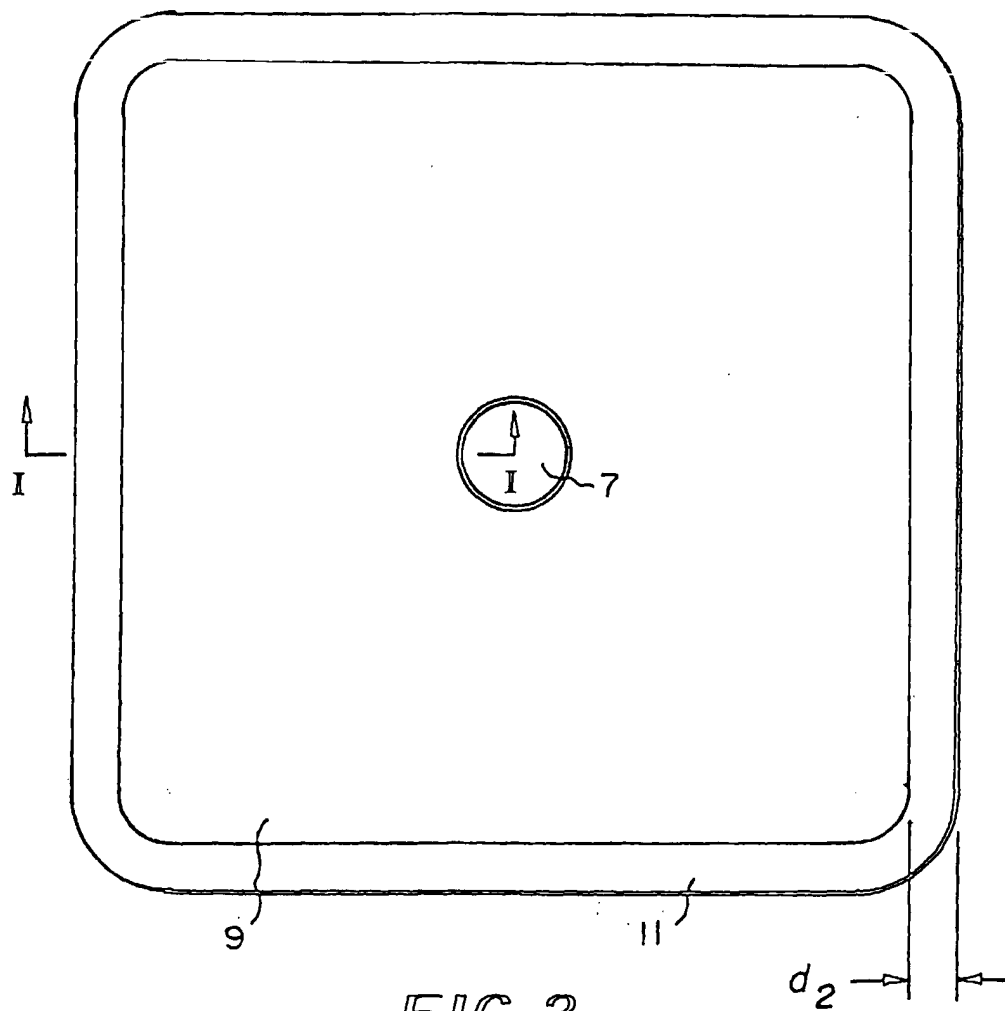


FIG. 1



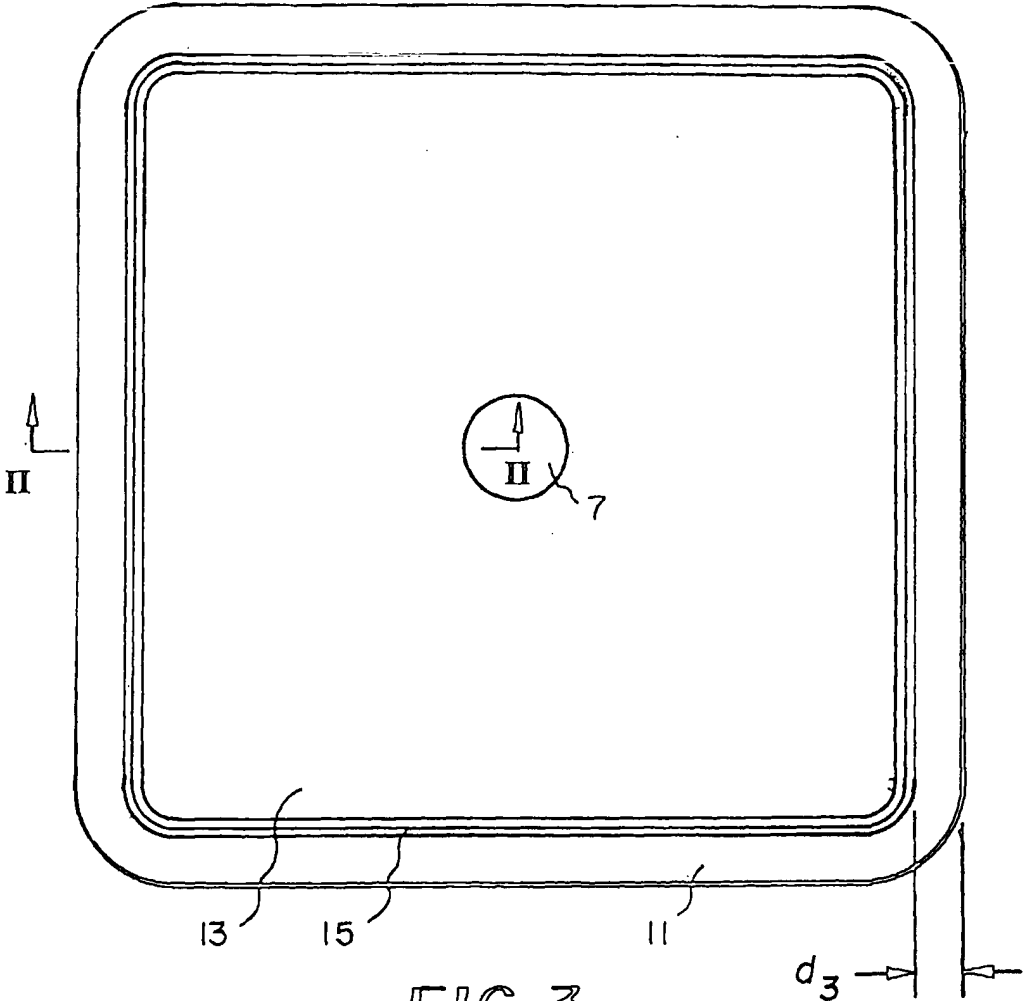


FIG. 3

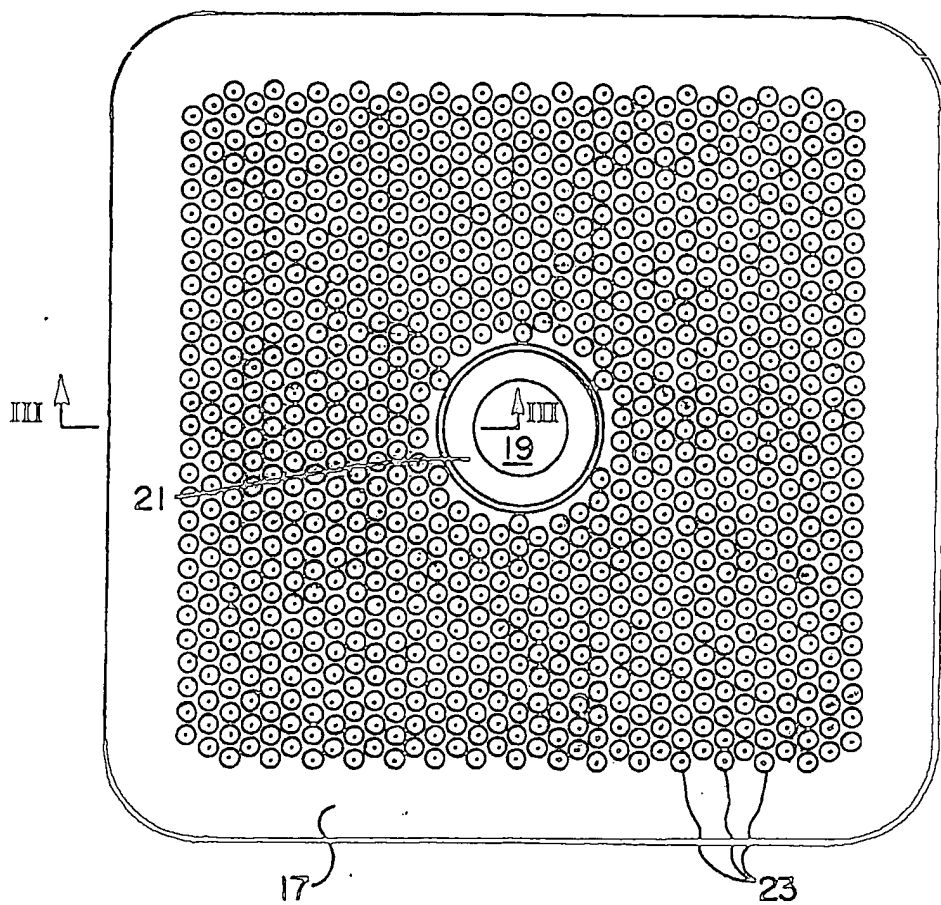


FIG. 4

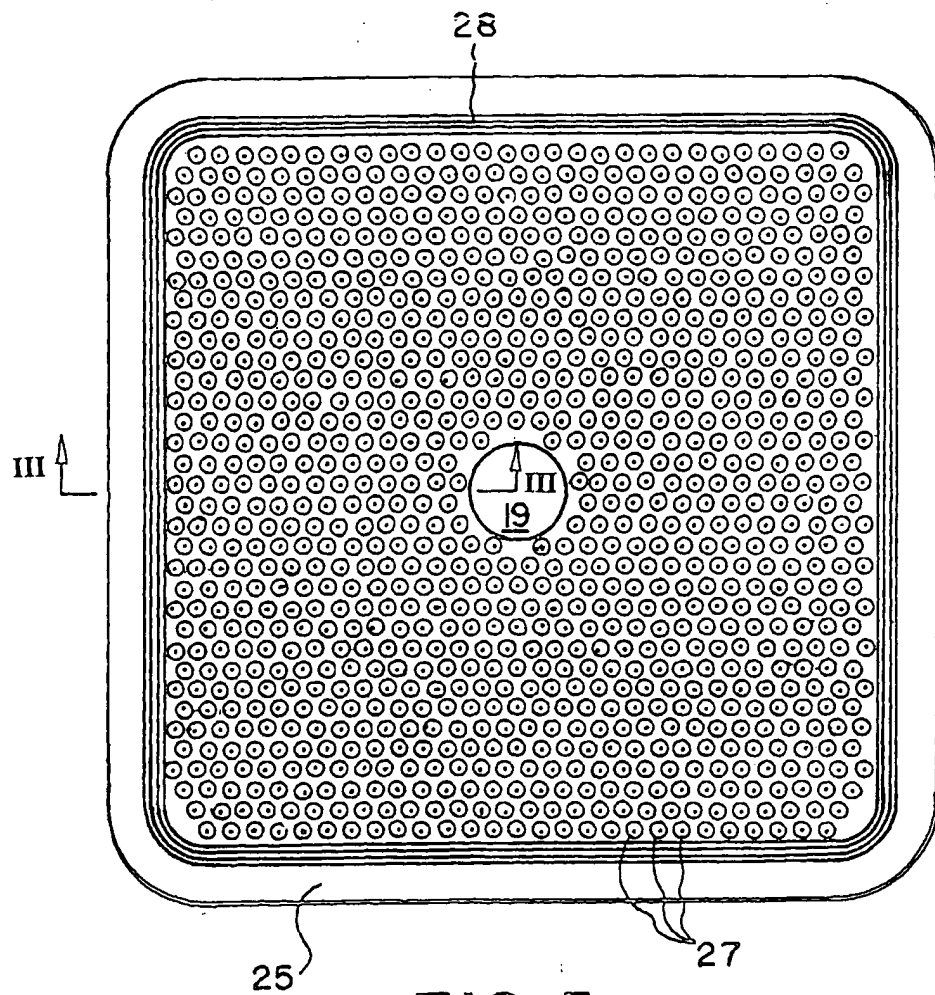
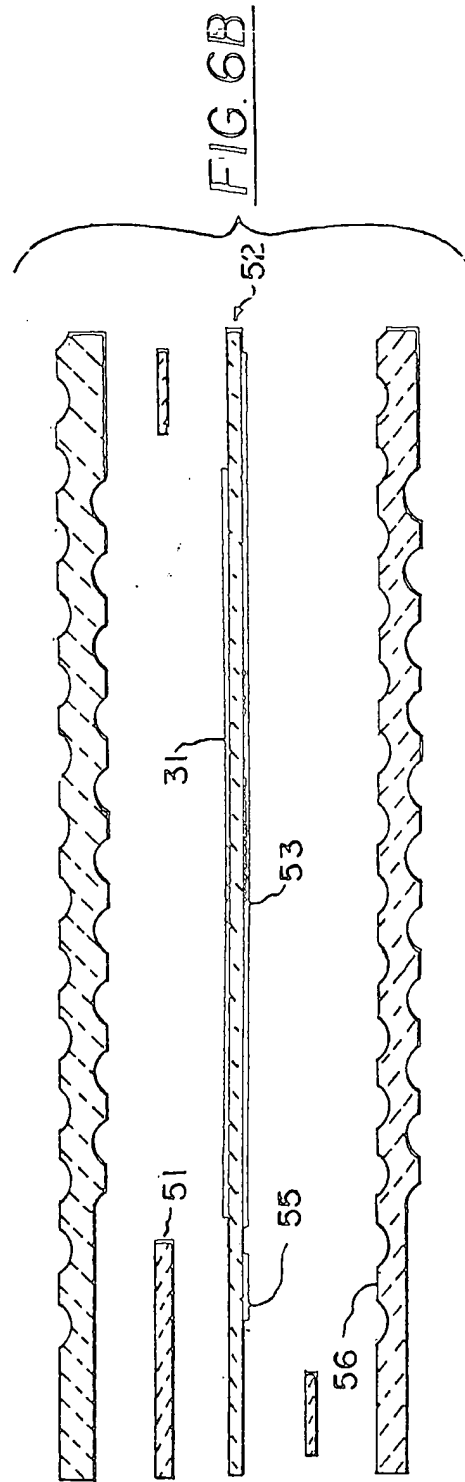
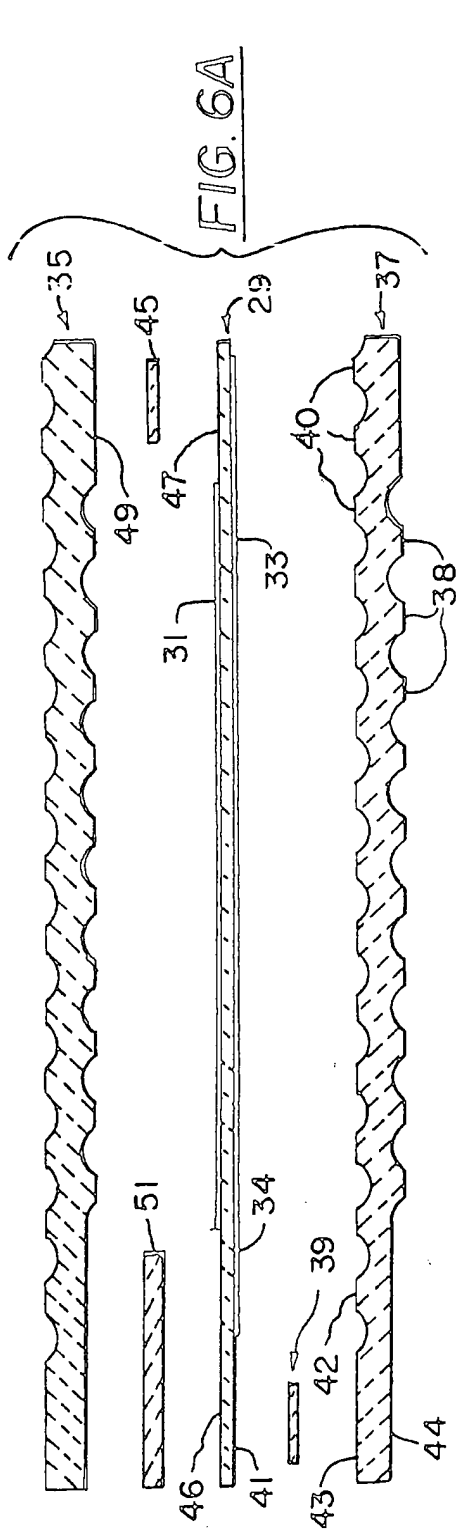
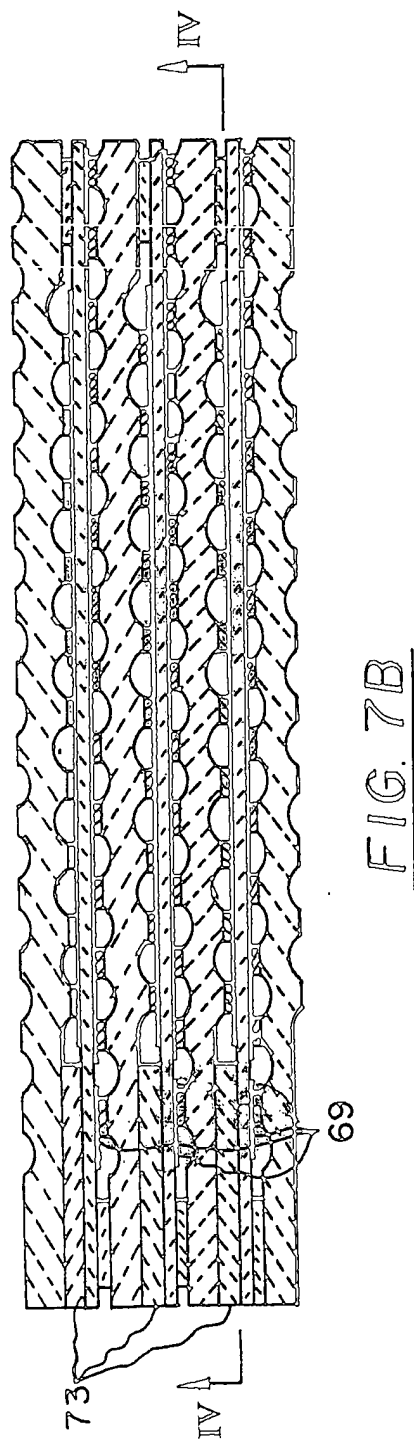
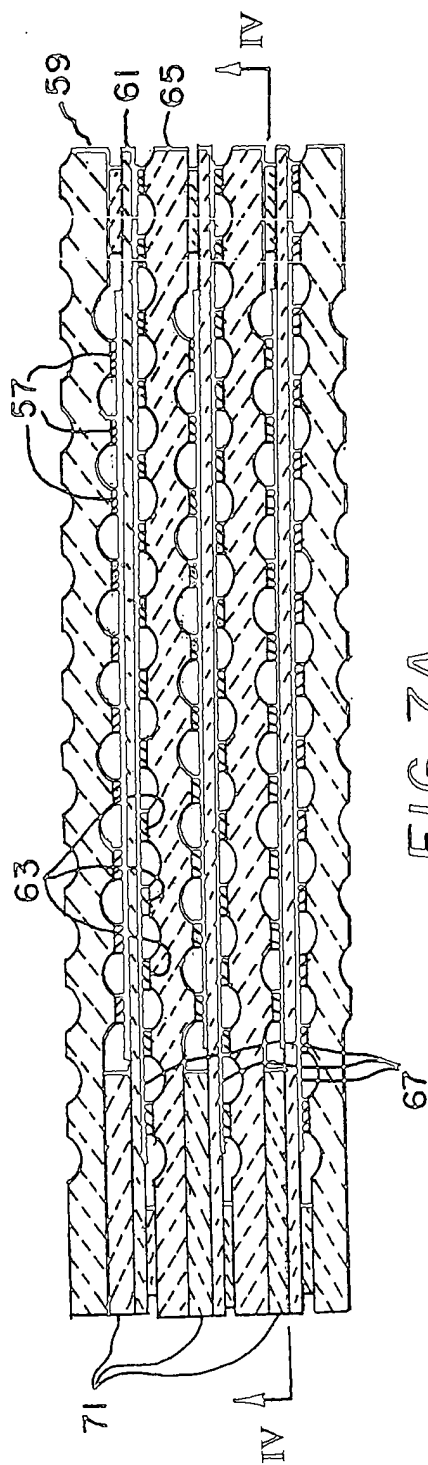


FIG. 5





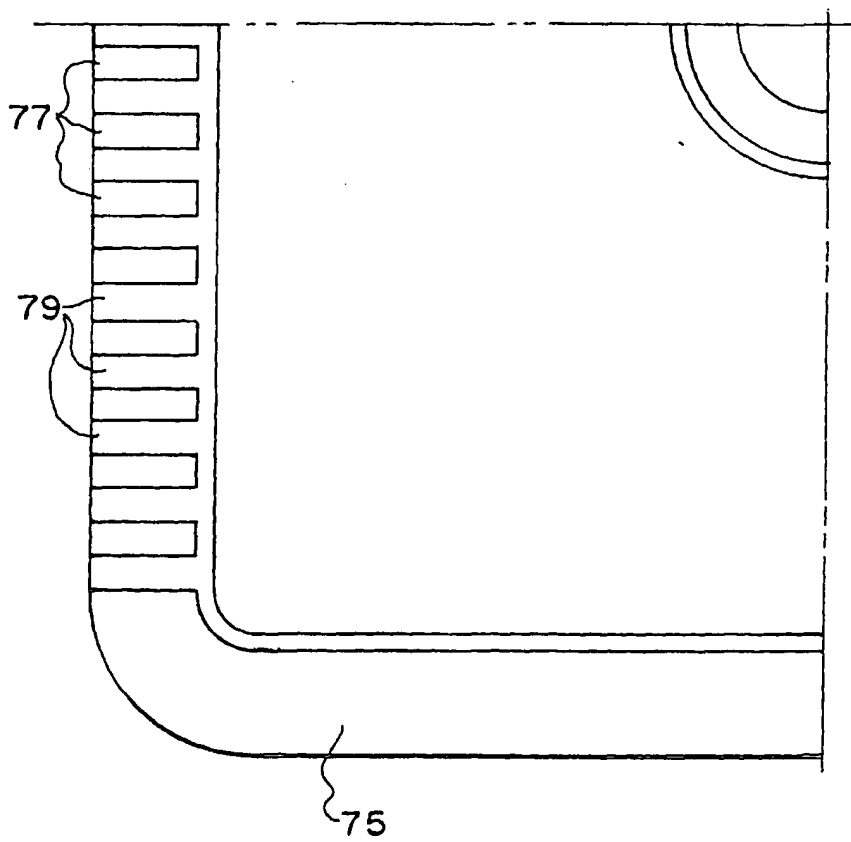


FIG. 8

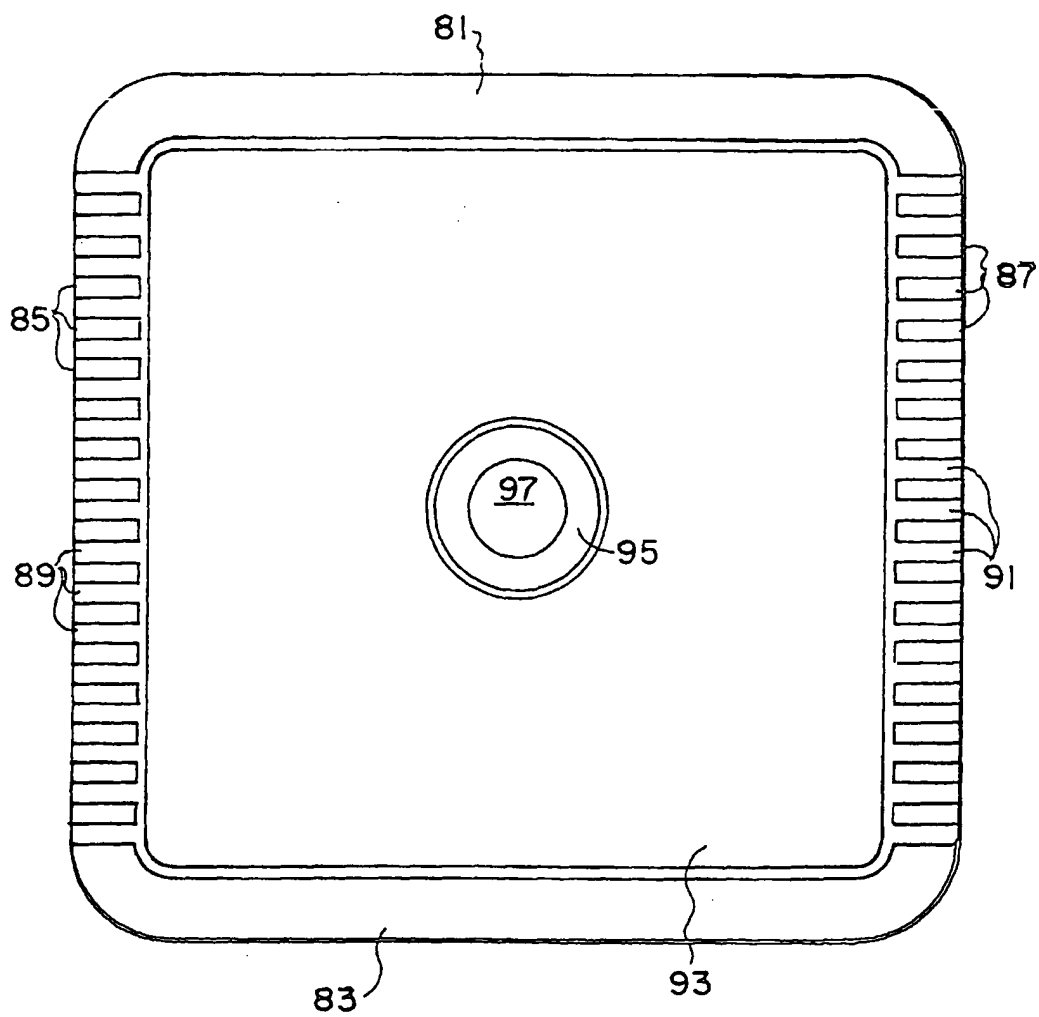
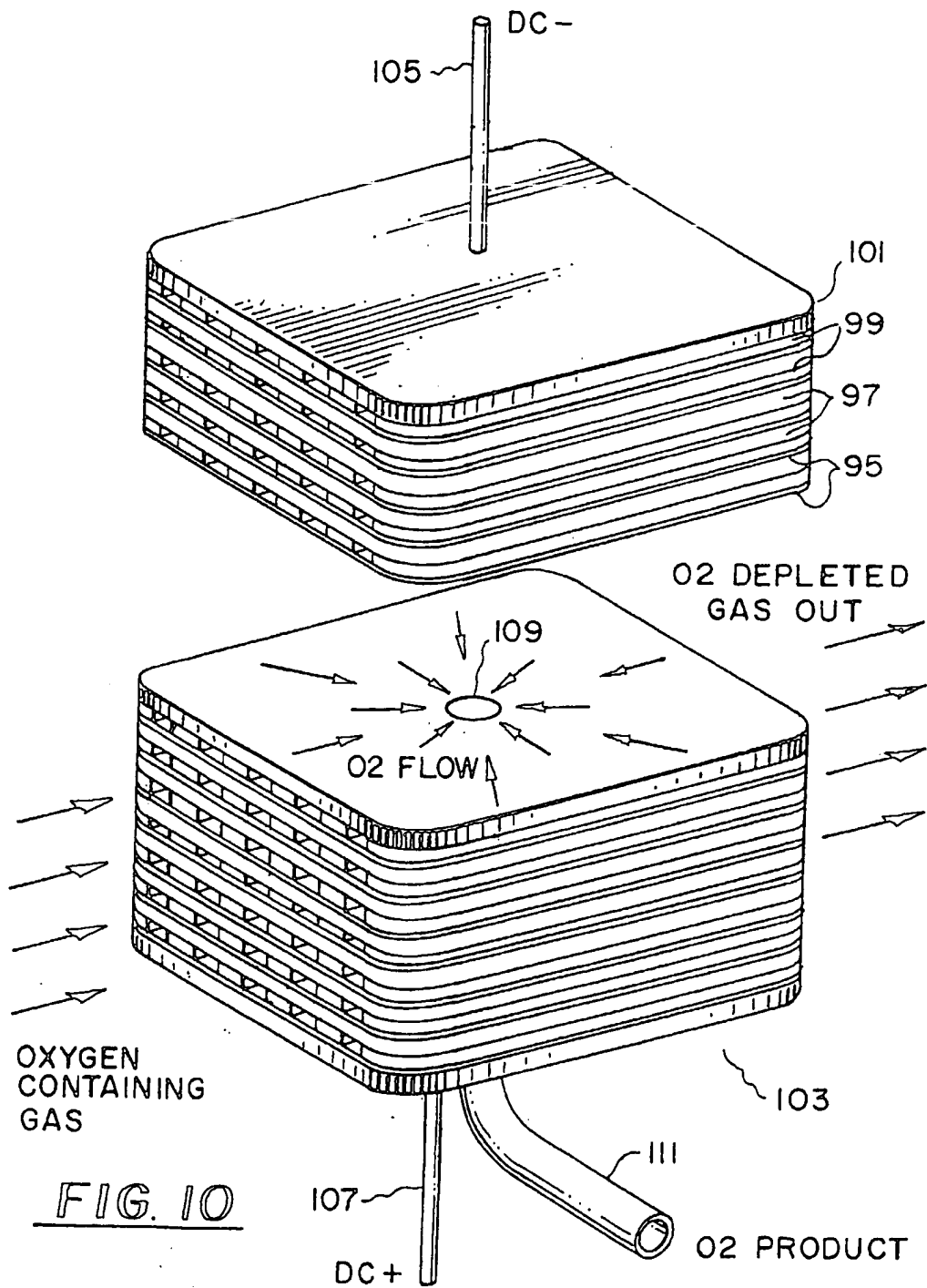


FIG. 9



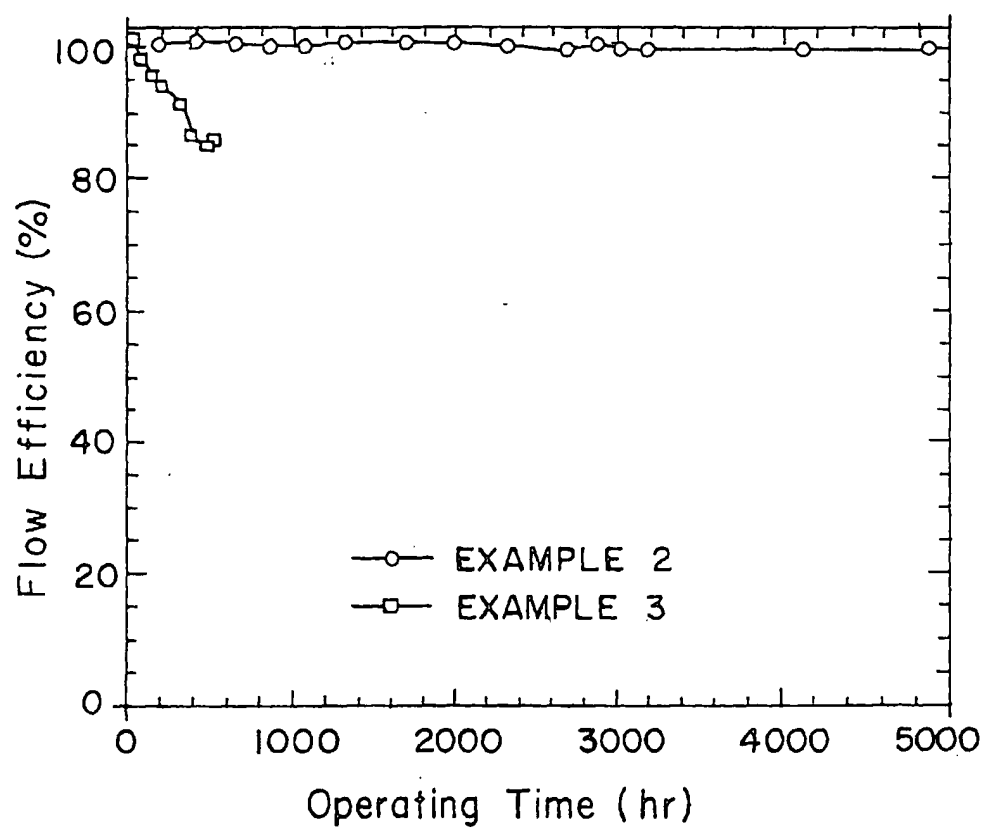
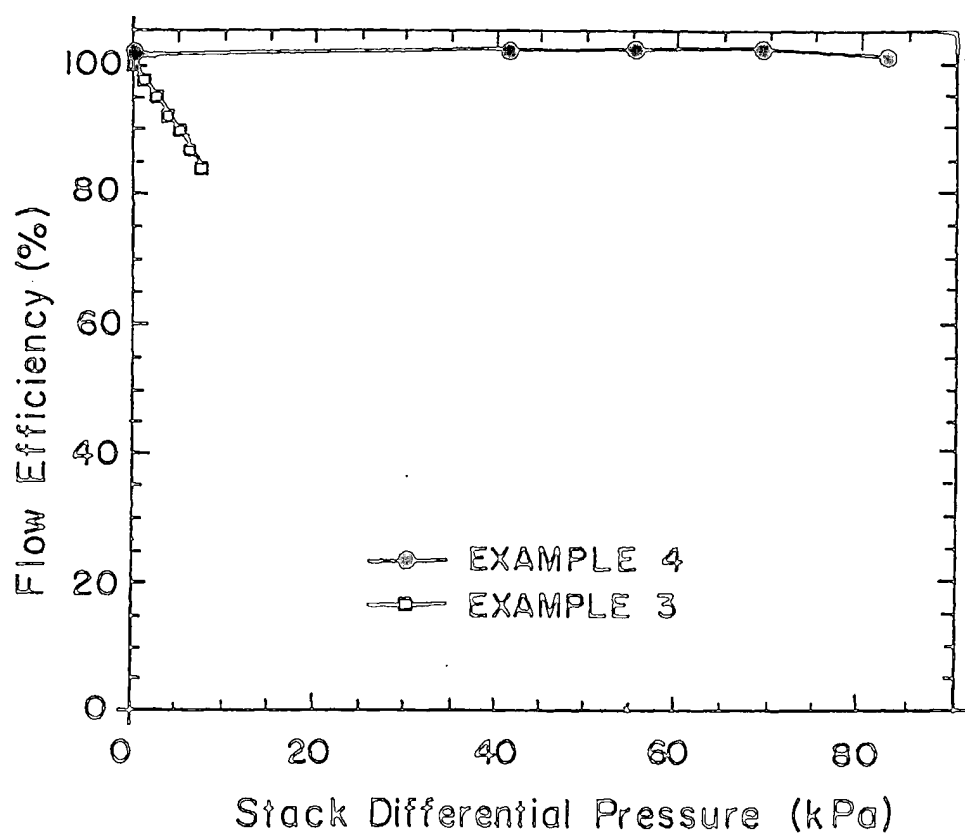


FIG. II

FIG. 12

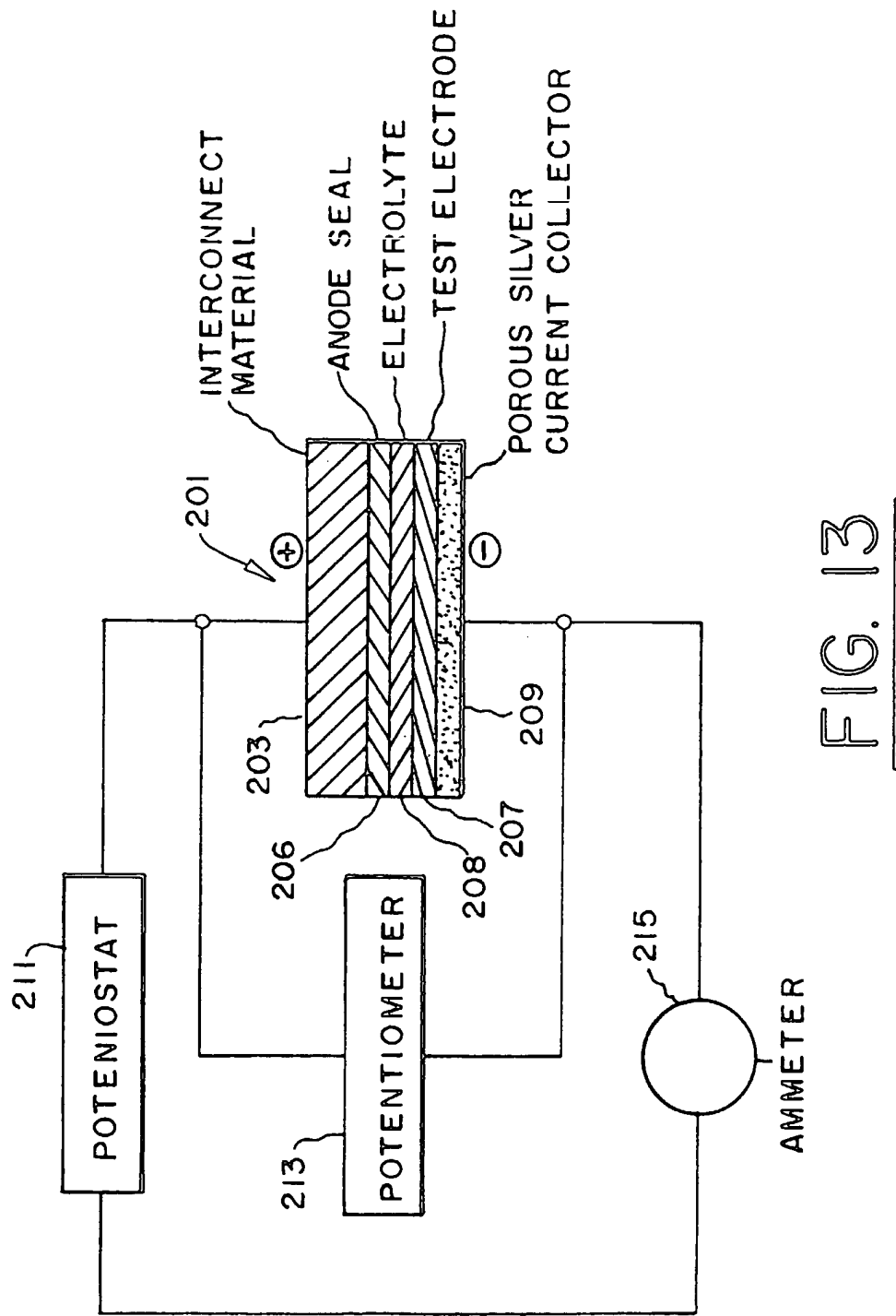


FIG. 13

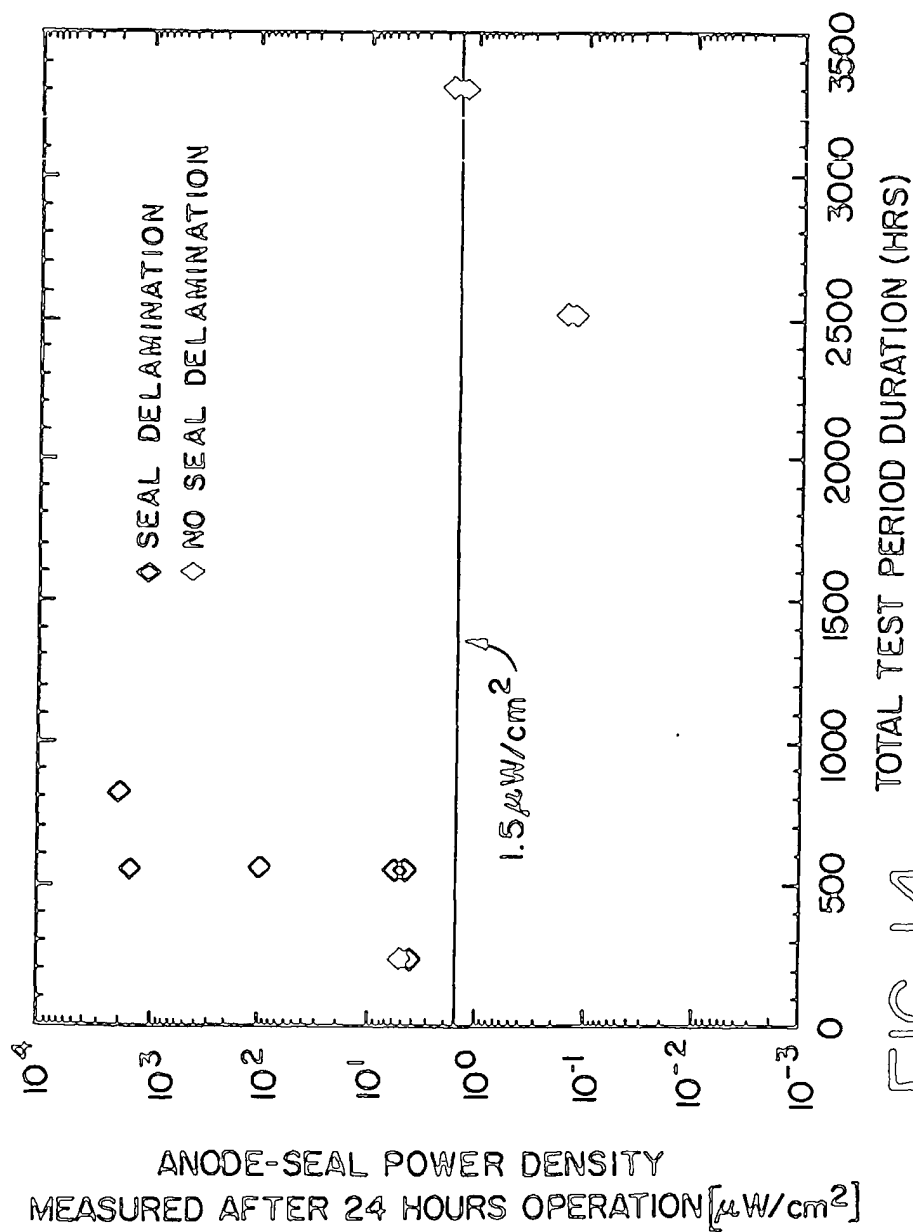
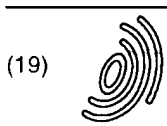


FIG. 14



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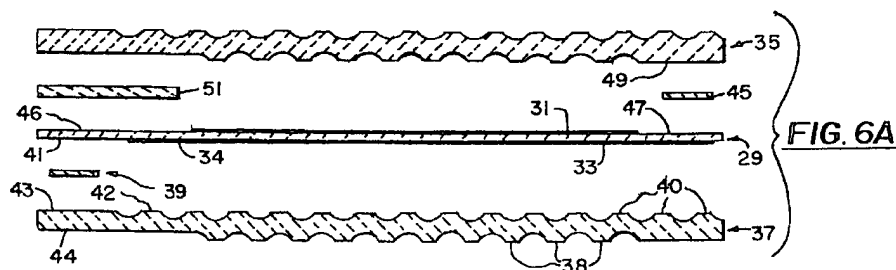
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(54) **Separation of oxygen from an oxygen-containing gas**

(57) An electrochemical device for separating oxygen from an oxygen-containing gas comprises a plurality of planar ion-conductive solid electrolyte plates and electrically-conductive gas-impermeable interconnects assembled in a multi-cell stack. Electrically-conductive anode and cathode material is applied to opposite sides of each electrolyte plate. A gas-tight anode seal is bonded between the anode side of each electrolyte plate and the anode side of the adjacent interconnect. A regulating electrode, applied to the anode side of each

electrolyte plate between the anode seal and the edge of the anode, eliminates anode seal failure by maintaining the 24-hour anode seal power density below about $1.5 \mu\text{W}/\text{cm}^2$. A gas-tight seal is applied between the cathode sides of each electrolyte plate and the adjacent interconnect such that the anode and cathode seals are radially offset on opposite sides of the plate. The combination of regulating electrodes and offset seals is particularly effective in eliminating anode seal failure.



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EUROPEAN SEARCH REPORT

Application Number
EP 99 11 6735

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 November 2000	Examiner Doolan, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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